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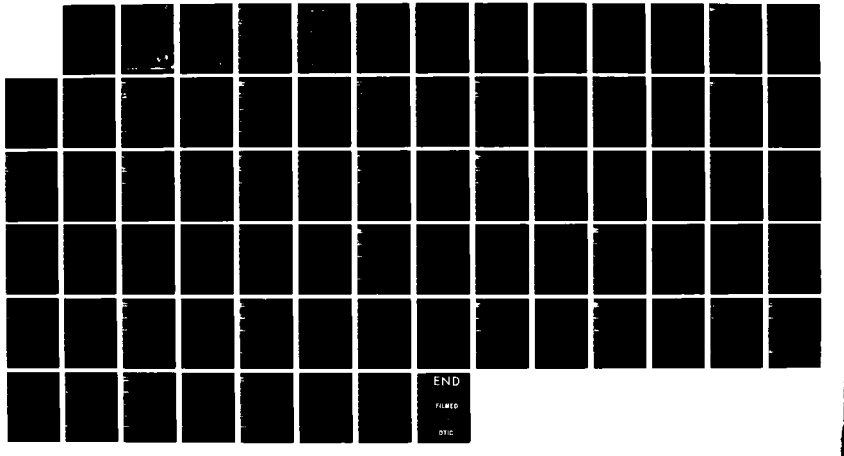

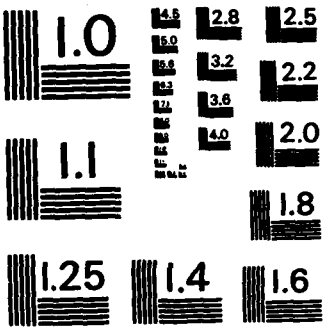

DIELECTRIC SPECTROSCOPY OF SEMICONDUCTORS

FINAL REPORT ON
US ARMY CONTRACT DAJA 37-81-C-0773

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and S H Zaidi

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

PART I DIELECTRIC SPECTROSCOPY OF SEMICONDUCTORS

Dielectric spectroscopy of semiconductors (DSS) employs dielectric measuring techniques to study delayed electronic transitions in and out of localised energy levels in the forbidden gap. Horizontal transitions between levels normally take place in the volume of the material and involve relatively small changes of energy. Vertical transitions between deep levels and the free bands involve energy changes of the order of half the band gap and take place

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20. continued. mainly in interfacial space charge regions and at semiconductor-metal interfaces. DSS is uniquely able to resolve the spectra of these delayed transitions and measurements on semi-insulating GaAs in the frequency range 10^{-2} - 10^{4} Hz and between 90 and 380 K show that none of them conforms to the expected exponential time dependence. The various transitions are found to have well recognisable spectral "signatures" involving fractional power law dependences on frequency and hence on time. The exponents are sensitive to the nature of the transitions and to the types of impurities and may also depend on the crystalline order. We report for the first time in the context of SI GaAs the phenomena of low-frequency dispersion both in the volume and in interfacial transitions, and also of negative capacitance, all of which involve some structural instabilities and the likelihood of electrochemical energy storage. We also show the existence of "electronic phase transitions" involving subtle reversible changes of electron-lattice interactions at well-defined temperatures. The power laws are associated by us with many-body interactions affecting the transitions in localised levels, which are not well understood probably on account hitherto of a lack of experimental evidence. This shows the usefulness of DSS as a unique technique for studies of semiconductor transitions.

PART II DIELECTRIC SPECTROSCOPY OF SCHOTTKY DIODES ON N-TYPE GaAS

Measurements are reported of the dielectric response in the frequency range 10^{-2} - 10^{4} Hz of Schottky diodes on n-type GaAs with aluminium metallisation, with the results revealing several important deviations from the classically expected response. The most important and unexpected phenomena are the appearance of low-frequency dispersion (LFD) and of negative capacitance, which are strongly influenced by even small (0.1V) negative and positive biases, respectively. Both phenomena are linked with interfacial processes involving some form of instability arising from structural transformations at the metal-semiconductor interface. Direct evidence of slow recovery over many hours after strong biasing supports this view. Time-domain measurements are reported in the range 10^{-4} - 10^{5}s, showing that the charging current under step-function forward biasing is *rising* over a certain time interval, while the reverse bias gives a continuously falling current. These observations are fully consistent with the appearance of negative capacitance and LFD. The steady state voltage-current characteristics also show very unusual behaviour which is inconsistent with the classical model of Schottky diodes. The conclusion is that the behaviour of Schottky diodes on GaAs is completely inconsistent with the normally accepted theories and requires a fresh approach to its interpretation.

PART I

DIELECTRIC SPECTROSCOPY OF SEMI-INSULATING GALLIUM ARSENIDE

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ABSTRACT

Dielectric spectroscopy of semiconductors (DSS) employs dielectric measuring techniques to study delayed electronic transitions in and out of localised energy levels in the forbidden gap. "Horizontal" transitions between levels normally take place in the volume of the material and involve relatively small changes of energy. "Vertical" transitions between deep levels and the free bands involve energy changes of the order of half the band gap and take place mainly in interfacial space charge regions and at semiconductor - metal interfaces. DSS is uniquely able to resolve the spectra of these delayed transitions and measurements on semi-insulating GaAs in the frequency range 10^{-2} - 10^{4} Hz and between 90 and 380K show that none of them conform to the expected exponential time dependence. The various transitions are found to have well recognisable spectral "signatures" involving fractional power law dependences on frequency and hence on time. The exponents are sensitive to the nature of the transitions and to the types of impurities and may also depend on the crystalline order. We report for the first time in the context of SI GaAs the phenomena of low-frequency dispersion both in the volume and in interfacial transitions, and also of negative capacitance, all of which involve some structural instabilities and the likelihood of electrochemical energy storage. We also show the existence of "electronic phase transitions" involving subtle reversible changes of electron-lattice interactions at well defined temperatures. The power laws are associated by us with many-body interactions affecting the transitions in localised levels, which are not well understood probably on account hitherto of lack of experimental evidence. This shows the usefulness of DSS as a unique technique for studies of semiconductor transitions.

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INTRODUCTION

The dielectric response of electronic semiconductors is normally associated with behaviour in the frequency range corresponding to lattice vibrational frequencies in the infra-red region of the spectrum, and with the various electronic excitation processes at higher frequencies, including plasma phenomena [1,2]. In keeping with this approach nothing is normally expected to happen dielectrically at lower frequencies and the low-frequency dielectric constant is accordingly taken to be equal to the high-frequency value ε_∞ which is equal to the square of the refractive index. It is noteworthy that there is no truly low-frequency measurement, say in the kHz region, of the permittivity of any of the common semiconductors such as silicon and the various III-V compounds because their high direct current (dc) conductivity σ_0 , even in intrinsic materials, causes the dielectric loss to be dominated by corresponding contribution σ_0/ω up to the MHz range. The accurate determination of the permittivity is very difficult against this high loss. On the other hand, the commonly made measurement of the capacitance of p-n junctions does not give the absolute value of ε because this would require the knowledge of the width of the space charge region which cannot be known with sufficient accuracy, so that in practice the measurement of capacitance of a p-n junction is used to determine its width by *assuming* that $\varepsilon = \varepsilon_\infty$.

The approach adopted in the present study is based on the proposition that a great deal is, in fact, happening dielectrically in semiconductors in which *delayed electronic transitions* make a significant contribution to the complex dielectric permittivity. We are able to measure this contribution even though we are unable to assign an exact valule to ε_∞ . The delayed transitions in question are predominantly those between deep levels in the forbidden gap and also between these levels and the free bands. The corresponding transition rates fall in the radio, audio and sub-audio frequencies, depending on the energy involved and on the temperature.

The experiments described in the present paper were carried out on semi-insulating (SI) GaAs , partly because its high resistivity makes dielectric measurements possible even at room temperature, and partly because of the considerable scientific and technological interest attaching to this material. Our measurements have shown that SI GaAs has some quite unique dielectric properties which set it apart from most other semiconductors.

Deep levels in semiconductors constitute one of the most important factors determining the properties of these materials, and at the same time they are relatively little understood, particularly if they involve complex imperfections consisting of more than one simple defect [3]. In view of this limited understanding of the physics of deep levels, they are normally being characterised in terms of their energy with respect to one or other of the free band edges and in terms of their probability of capturing an electron or a hole from the free bands. This probability is often expressed as the capture cross-section Σ, which expresses the probability of capture of a free carrier moving with a thermal velocity v_{th} as $P = \Sigma v_{th}$. This capture probability, multiplied by the density of the non-interacting free carriers, gives the net trapping rate in a centre and this, in turn, determines the equilibrium rate of detrapping or release of a carrier from the centre. Defined as a steady state property, this detrapping rate R is taken to determine the rate of release of carriers trapped under non-equilibrium conditions after the removal of a generation process, so that the number n_t of occupied traps is given as function of time after the removal of excitation by the differential equation:

$$dn_t/dt = -Rn_t \qquad (1)$$

which leads to the expectation of an exponential detrapping process with a rate constant R from an initial excess density n_{to}:

$$n_t(t) = n_{to}\exp(-R\,t) \qquad (2)$$

The experimental evidence presented in this paper will prove conclusively that this normally expected exponential time dependence of trapped carrier density is not being followed, the actually applicable rate being a power law in time. The present experimental data are not the only pointer in the direction of non-applicability of exponential time dependence - similar conclusions were obtained from a careful examination of the experimental data relating to the time dependence of luminescence in a wide range of solids [4], where power laws were found to be generally applicable.

There is no accepted interpretation of the significance of these power law relations in trapping processes, but the suggestion is that these laws are the consequence of many-body interactions, rather on the lines of the corresponding relations found in dipolar dielectric relaxation for which a strict theoretical analysis in terms of many-body processes

has been developed by Dissado and Hill [5] .

Experimental determination of the various transition rates consists in the introduction of some non-equilibrium condition, for example by optical generation of carriers in the case of photoconductivity, or by suitable biasing of a p-n junction and the subsequent determination of the rate of change of capacitance. These experiments are being performed in real time and this imposes severe limitation on the range of times which may be explored, so that it is not easy to obtain reliable information on the exact time dependence of the processes in question. An alternative approach has been developed in our Group consisting in the application of a periodic excitation rate to a photoconductor and simultanous measurement of the excess photoconduction as function of the frequency of the excitation. This method has the advantage of giving a very wide range of frequencies and also of being independent of any dark current [6] but this subject will not be covered in the present paper.

DIELECTRIC SPECTRA OF ELECTRONIC TRANSITIONS

The "dielectric" method of determining the transition rates consists in the introduction of a slight perturbation resulting from the application of an alternating signal to a sample which may be homogeneous, in which case one is looking at volume processes, or may contain a space charge region near one or both electrodes which then determines the interfacial rates. Charges making transitions between localised levels act in a manner similar to dipoles turning abruptly between preferred positions and since these transitions are delayed with respect to the exciting signal they register as a complex dielectric permittivity [7].

For the purpose of the following discussion it will be advantageous to distinguish between "*vertical*" and "*horizontal*" transitions which are illustrated in Figure 1, the former being transitions between localised deep levels and the free bands, the latter taking place mainly between the localised levels themselves. Vertical transitions involve relatively large changes of energy compared with horizontal ones and this energy has to come from thermal excitation or from optical excitations for upwards transitions, while downward transitions must dispose of the corresponding amounts of energy, either non-radiatively to the lattice or radiatively in the case of luminescent response. Because of the large amounts of energy required, the vertical transitions may be delayed significantly with respect to the primary excitation and even horizontal transitions give easily measurable delays which register as

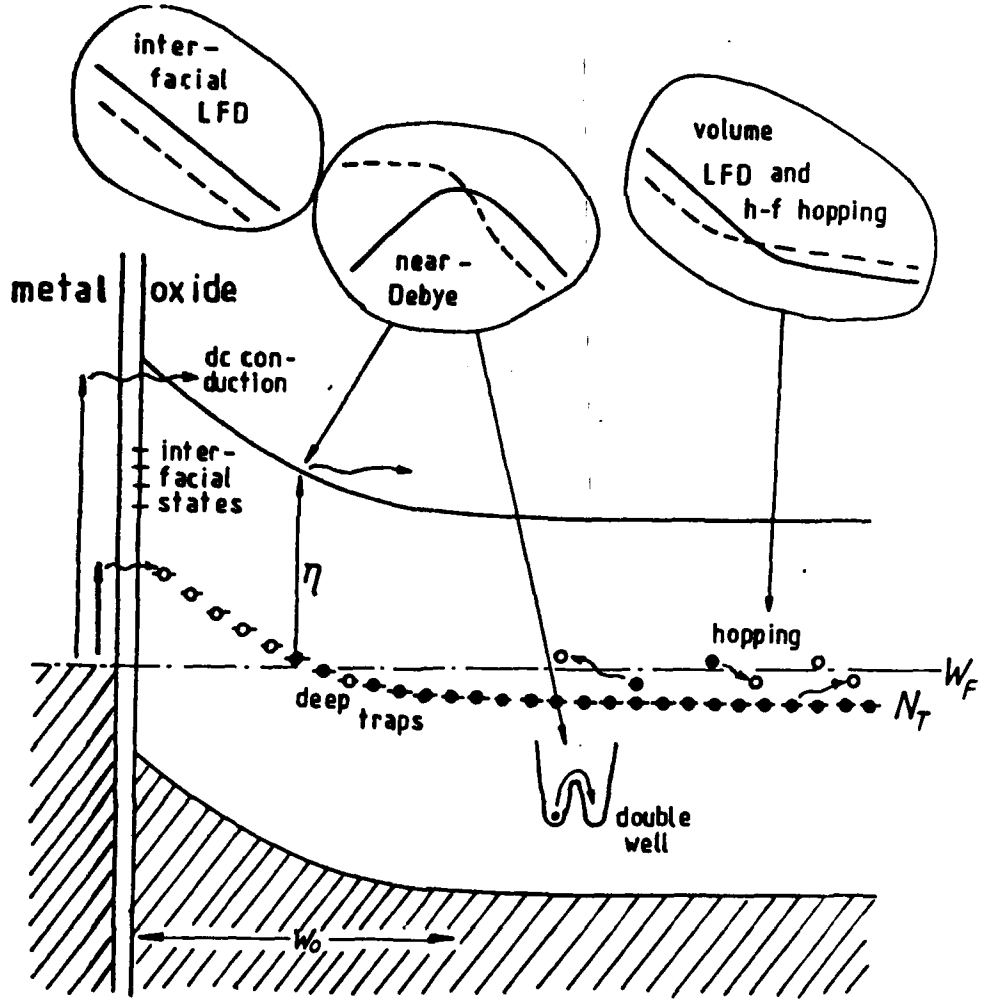

Figure 1

A schematic representation of the band structure and localised levels in a semi-insulator near an interface with a metal . The Fermi level W_F is deep in the forbidden gap an a set of N_T deep traps is shown at an energy η below the conduction band. A potential double well is shown to represent an electron or an ion constrained to hop between two localised allowed positions. Extended hopping near the Fermi level is shown. In the space charge region emission and capture of electrons takes place near the cross-over of the Fermi level with the trapping states. At the interface an oxide layer is shown with interfacial states. Various electronic transitions are shown by arrows. The diagrams in contours show the various dielectric responses in logarithmic coordinates for $C'(\omega)$ (-----) and $C''(\omega)$ (———) corresponding to the various types of transitions .

dielectric loss in the appropriate frequency range.

With reference to the vertical transitions, we have noted that the generally expected time dependence of the return to equilibrium is exponential with the time constant corresponding to the relevant transition probability, or capture cross-section . In the frequency domain this would give rise to a purely Debye form of response, although we shall see that the observed behaviour deviates markedly from this ideal, conforming instead to the empirical Cole-Cole form [8] for the complex dielectric susceptibility

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \frac{\Delta\chi}{1 + (i\omega/\omega_p)^{1-n}} \qquad (3)$$

where ω_p is the loss peak frequency equal to R in eqn (2). $\Delta\chi$ is the low-frequency limit of the susceptibility increment due to this process and the exponent n determines the degree of deviation from the ideal Debye response for which $n = 0$. For values of the exponent $n < 0.3$, say, the behaviour may be described as "near-Debye", but with the important property that the high-frequency response is characterised by a power-law dependence:

$$\chi(\omega) = \Delta\chi(i\omega)^{n-1} = \Delta\chi[\sin(n\pi/2) - i\cos(n\pi/2)]\omega^{n-1} \qquad (4)$$

in which the real and imaginary components of χ follow the same frequency dependence with a constant ratio

$$\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2) \qquad \omega \gg \omega_p \qquad (5)$$

This is known as the "universal" law of dielectric response [7] since it is found in virtually all dielectric systems with either dipolar or charge carrier polarisation and it is very interesting to find that it is also obeyed by systems in which the dominant influence on polarisation is trapping dynamics.

The power law relation (4) corresponds to the time-dependence of the charging and discharging currents which is its Fourier transform :

$$i(t) \propto t^{-n} \qquad (6)$$

which is completely different from the exponential dependence corresponding to the Debye law which represents a singularity for the limit $n = 0$ in which the high-frequency behaviour is given by

$$\chi'(\omega) \propto \omega^{-2} \qquad \chi''(\omega) \propto \omega^{-1} \qquad (7)$$

which cannot be mistaken for the universal law (4).

The near-Debye response is expected in systems dominated by dipolar interactions in dielectric polarisation or by release of charges from deep traps in semiconductor situations [7], since in both cases there is a limited amount of charge available in the system - once the dipoles have re-oriented themselves or the trapped charge has been released there is no forther contribution to polarisation. The situation is completely different in systems where extended charge carrier movements are possible by hopping processes, in which case the high-frequency behaviour is still the same as that given by eqn (4) , but with generally larger values of the exponent , n = 0.6 - 0.9 , say , while the low-frequency response becomes dominated by the same type of law but with a very much smaller exponent n , similar to that seen in the high-frequency branch of near-Debye behaviour. This is known as Low-Frequency Dispersion(LFD)[7,9,10] and it can give rise to very high values of susceptibility and of capacitance, several decades above the high-frequency values. The corresponding time-domain behaviour follows the same type of law as given by eqn (6), but with the small exponent this law becomes almost independent of time, giving the appearance of steady current, but with the discharge currrent following the same dependence. The implications of this type of behaviour are that the energy is being stored in the system not electrostatically, as in dipolar polarisation but electrochemically [10,11] and the implication is that structural changes may be taking place in the system . A theory of LFD behaviour has been developed by Dissado and Hill [12] on the basis of many-body interactions in the volume of the material in which "incomplete dc transport" is taking place, charges being prevented from freely crossing the sample from one electrode to the other and very high polarisation taking place instead. The behaviour differs from the classical Maxwell-Wagner process [10] in which blocking barriers give rise to large polarisations but the behaviour there is modelled by series R - C combinations which should give Debye characteristics so that the only way of reconciling theory with experiment is by postulating the existence of large distributions of parameters. However, as with similar distributions of relaxation times in dipolar polarisation, the ultimate question of the credibility of these distributions has to be asked, since the end result is a well defined power law for which there is now a good many-body theory also by Dissado and Hill [5] . In our view, the LFD behaviour reported in the present paper is not consistent with the Maxwell-Wagner interpretation.

A clear distinction should be made between the dispersive behaviour at the high-frequency end of a near-Debye loss process and the LFD response

arising from extended charge carrier movements. The differences appear in the behaviour at low frequencies - the near-Debye response must show a saturated value of the real part of the susceptibility, the LFD has no such natural termination in its own right, although more will be said about this later. There is also a very important difference in the absolute values of the low-frequency limit of the permittivity - in the "dipole-like" near-Debye response this is not large in comparison with ε_∞ , since it is difficult to achieve such large polarisations from trapping centres in the bulk material.

The high-frequency component of the carrier response given by eqn (4) with the higher values of the exponent, and therefore corresponding to the less dispersive part of the spectral shape of $\chi(\omega)$ has a well known counterpart in the alternating-current conductivity $\sigma(\omega)$ found in many materials in which electronic hopping conduction is the dominant polarisation process . It is generally accepted that the empirical relation is applicable [13] :

$$\sigma(\omega) = \varepsilon_0 \chi''(\omega) \quad \propto \omega^n \tag{8}$$

and this is exactly the same as for the high-frequency dipolar behaviour.

The status of the theoretical understanding of the frequency dependence of dielectric responses of various systems should be clearly understood. The Dissado-Hill theory of many-body dielectric response [5] is strictly valid for dipolar polarisation and it is clear that no molecular dipoles exist in typical semiconductors and certainly not in GaAs. Dipole-like behaviour is expected of electrons or ions hopping between two allowed positions - in potential double wells. Such electronic or ionic dipoles would be expected to follow the same theory. There is less certainty about the applicability of this theory to extended hopping which results the high-frequency ac conductivity of eqn (8). There is, however, no theoretical justification at the present time for the observed frequency dependence of the trapping processes - these facts are being simply reported here as observations from experimental studies and no attempt is being made to find a theoretical justification for them.

INTRODUCTION TO BARRIER RESPONSES

A significant fraction of our experimental data indicate strong dispersions which may be clearly associated with barrier phenomena, as distinct from distributed volume processes and it is important to outline the general theory of this type of behaviour to facilitate orientation in the experi

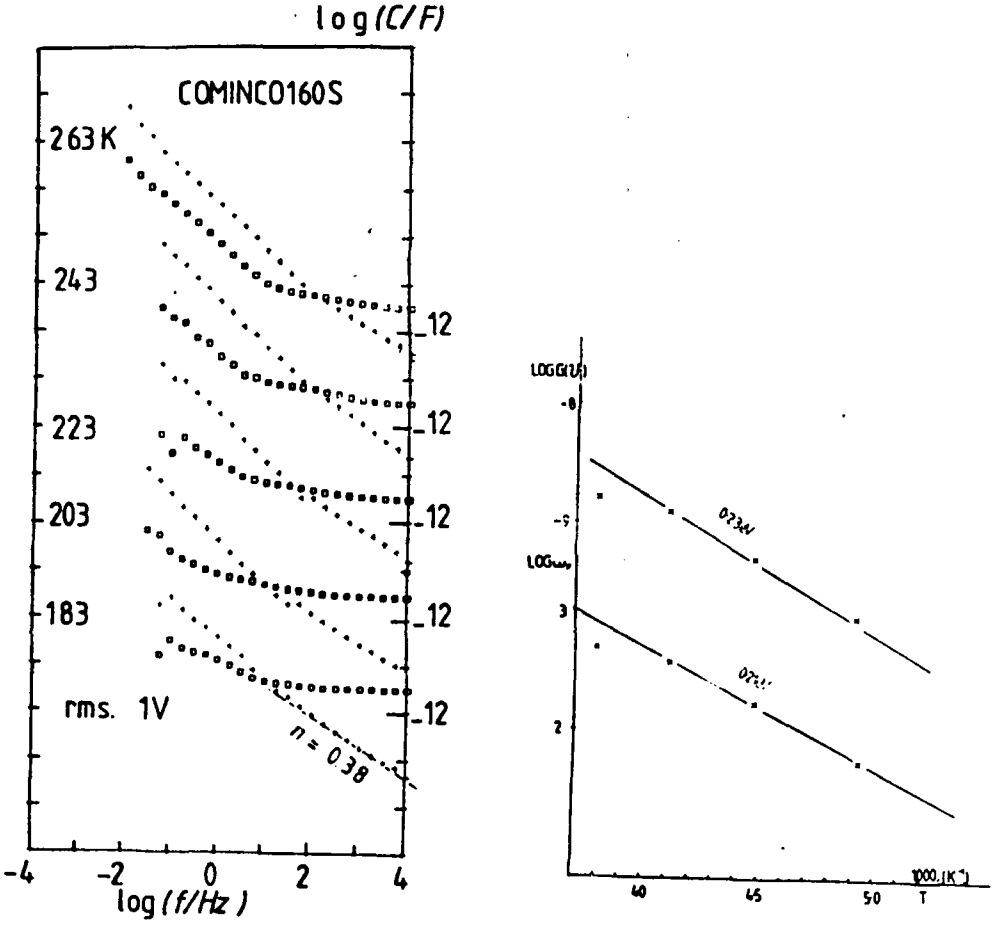

Figure 6

The dielectric response of a sample of undoped GaAs Cominco 160S for a range of temperatures 183 - 263K, showing in diagram a) the gradual evolution of LFD with increasing temperature, together with a small dispersion moving with temperature towards higher frequencies. The inset shows , diagram b) , the activation energy plots for the frequency shift and dc conductivity.

connected and one interpretation may be that they correspond to hopping between levels reasonably close to the Fermi level and at an energy separation of ≈ 0.1 eV, the reciprocating motions which predominate giving rise to the loss peak process, while the onward movement of the same carriers produces the dc contribution. The reciprocating movements cannot be of the simple double-well hopping type, since these would be expected to be closer to Debye in their characteristic - it may be that several centres at a time are involved.

The close relation between the dc loss G_0/ω and of the capacitance dispersion is common to most of our samples , with the further feature also visible clearly in other samples that the dc and frequency shift activation energies are slightly different, the latter being smaller. At higher temperatures the activation energy for G_0 becomes much larger, indicating the onset of another competing mechanism, while that for ω_p remains the same, since there is no alternative process to the reciprocating motions between "favoured pairs".

The value of the exponent n = 0.36 - 0.40 , according to normalisation, is not compatible with a typical near-Debye process and it is certainly not consistent with typical extended hopping , which would require values closer to 0.6-0.8. It cannot be interpreted as bulk LFD, since there is a clear saturation of $C'(\omega)$ at low frequencies, so we have to conclude that this is the manifestation of a loss peak process due to dipole-like hopping between pairs.

We note that the $C'(\omega)$ data show a clear up-turn at the lowest frequencies at 240 K , marking the onset of a high-temperature process which will become well pronounced in Figure 11 , where it will be associated with barrier dispersion.

A similar behaviour is seen in an undoped Cominco 160 sample shown in Figure 6a) in the temperature range 183-263K. The complicating feature here is the presence of LFD which has a temperature-dependent value of the exponent n as is seen especially clearly from the variable ratio C''/C' . The activation energies shown in diagram b) are significantly higher than for Cr-B , being 0.23 and 0.21 eV. While these energies are higher by a factor of three, they are still more compatible with volume processes than with typical barrier processes. It is not possible at this stage to pronounce definitely on the nature of the LFD process but the low activation energy supports the view that this is a volume transport mechanism, with the dispersion of $C'(\omega)$ covering 2½ decades without any sign of saturation.

the material does not undergo any phase transitions under the action of temperature, or where no secondary processes come into play , for instance under the applied steady bias.

It will be found, however, that in many of our data sets normalisation cannot be applied because the spectral shape of the individual sets corresponding to different temperatures etc, changes either continuously or abruptly. Under these condictions we are forced to conclude that the system itself changes under the action of the external constraint and this brings with it the changes of spectra. In such situations we display the data for individual temperatures etc as separate sets but we displace them vertically for clarity and ease of comparison. The information about deviations from a master curve can be as valuable in its own right as the applicability of normalisation is in other respects.

In many cases it is advisable to obtain a fitting of the data to simple "circuit" configurations comprising generalised frequency-dependent capacitors and resistors . A computer program has been devised [27] and this offers a means of rapidly fitting the data and obtaining the relevant parameters. Examples of this procedure will be given in some of our data sets.

We begin the presentation of our experimental data with volume responses which are generally found at low temperatures and in low-conductivity samples in which surface barriers play a relatively insignificant role. In the second place, we shall present data which are dominated by barrier phenomena, even though volume responses can also be discerned in them.

VOLUME DIELECTRIC RESPONSES

Our first example of a volume response in SI GaAs is shown in Figure 5 which relates to a Cr-doped sample referred to as Cr-B. Diagram a) gives the raw data for a range of temperatures 125-240K, displaced with respect to one another by two decades for clarity. The value of C_∞ is well compatible with the geometry of the sample and $C'(\omega)$ shows a slight dispersion moving to higher frequencies with increasing temperature. At high frequencies the loss has a value $n = 0.36$, i.e. very distinctly non-Debye , below the dispersion in $C'(\omega)$ the loss slope is -1 suggesting domination by dc conductance. A normalisation of $C(\omega)$ after subtraction of C_∞ is shown in Figure 5b) and the activation energy for frequency shift is shown in Figure 5c) as 0.08eV for C_0 and 0.07eV for ω_p . This suggests that the two processes are physically closely

if required, for example the subtraction of C_∞ and of the dc contribution.

On the whole, we were able to ascertain good reproducibility of results after even prolonged storage, after temperature cycling and even after removal and re-application of contacts. There is no evidence that surface leakage affects the measurements in the vacuum cryostat , as was ascertained in some cases by the use of guard ring structures.

PRESENTATION OF RESULTS

All our experimental data are presented in the first instance as logarithmic plots of $C'(\omega)$ and $C''(\omega)$ from which the effective dielectric susceptibility $\tilde{C}(\omega)$ can be obtained using eqn (9) . The use of capacitance instead of permittivity or susceptibility is preferred in view of the uncertainty with regard to the geometrical factor A/ω, particularly when the volume response is replaced by barrier response.

In many cases we apply the normalisation technique consisting in translation of data corresponding to various temperatures or dc biases or signal amplitudes along the logarithmic frequency and amplitude axes to obtain the "best fit" to a master curve and noting the locus of translation of a representative point on the original data [6,26]. The purpose of normalisation may be two-fold. Where the individual data sets can be brought into a single master curve, the behaviour may be specified in terms of a master equation

$$C(\omega,T) = \hat{A}(T)\, F(x) \quad \text{where} \quad x = \omega/\omega_p(T) \tag{15}$$

with $F(x)$ representing the *spectral shape function* of the reduced frequency variable and $\hat{A}(T)$ being the corresponding amplitude factor as function of temperature. In all these equations the parameter T may be replaced by any other variable, e.g. bias. Where a master curve $F(x)$ can be obtained , it gives a more reliable measure of the behaviour of the sample than do the individual constituent sets of data and also enables the activation energy for frequency shift to be obtained from the plot of $\log\omega_p(T)$ against $1/T$, if this gives a straight line relation, alternatively it provides information about departures from the activated behaviour, e.g. where tunnelling may become important.

To the extent to which normalisation is possible, one may conclude that the variation of the external parameter does not affect the nature of the interactions determining the spectral shape of the response, only the rates themselves are being changed. This is typically the case where

temperature these workers were able to show that the spectra of deep level emission deviate quite appreciably from the Debye shape corresponding to exponential time dependence. Using the fact that semiconductors such as silicon and gallium arsenide do not undergo structural phase transitions, they were able to show the gradual evolution of spectra for levels of various depths , where more than one level is present in significant density. However, admittance spectroscopy of p-n junctions is again incapable of furnishing information on the properties of the bulk extrinsic p- and n- regions which are relatively very conducting and do not contribute to the overall dielectric spectra.

The guiding principle in the application of DSS to the study of semi-insulating materials was the ability to obtain dielectric information pertaining to the volume of the homogeneous material, in addition to any contributions from space charge regions present near the electrodes. In this respect DSS constitutes an advance on the other methods since it is uniquely capable of looking in detail at the horizontal transitions in the bulk materials as well as the vertical transitions in the space charge regions. By offering a wide spectral range - after normalisation with respect to temperature, spectra of up to ten decades of frequency can be determined - the method provides a unique insight into the rate processes and their temporal development.

EXPERIMENTAL DETAILS

All our experiments were performed on samples in the form of wafers with suitable electrodes on opposite sides, placed in a vacuum cryostat with temperature control to ± 0.5K using a platinum resistance thermometer and a Eurotherm temperature controller. The samples were mounted with a heat sinking compound on the copper base of the sample holder.

Electrodes were applied either in the form of silver paint or evaporated aluminium , but in some cases preliminary ion bombardment implants were used to produce what is believed to be "ohmic" contacts. Details of dimensions and of electrodes of all samples used are shown in Table I .

Dielectric measurements were performed on a specially adapted Solartron Frequency Response Analyser (FRA) [25] covering the range 10^{-4} - 10^{4} Hz in a fully automated sweep, although the lowest two decades were seldom used. The presentation of data is automatic in the form of log-log plots of the real and imaginary components of the complex capacitance against frequency, and numerical data are available for further processing

An important development of both these techniques is the Deep Level Transient Spectroscopy (DLTS) [22] which adopts the dynamic approach of monitoring the time development of the changing capacitance under the action of depletion of trapped charges. This method can give information on energy and on capture cross-section of deep levels and it constitutes the most advanced form of the existing accepted techniques. Its limitation is the frequently poor signal-to-noise ratio.

All these techniques are essentially limited to the study of what we refer to in the present paper as the vertical transitions, because only these are capable of giving distinctive signals under conditions of excitation by some external agency. The second limitation of all these methods is that they are inherently not suited to the detailed study of time- or frequency-development of the charge release processes - they normally have to *assume*, explicitly or implicitly, an exponential law and they cannot therefore furnish any information on the detailed dynamics of trapping and detrapping processes. We shall see from the results quoted in the present paper that deviations from exponential time dependence are very significant in their own right and that the spectral shape of their response provides important information about the physical processes involved.

Both TSCap and DLTS techniques are inherently limited to the study of space charge regions in p-n junctions and Schottky diodes, they cannot provide any information about uniform bulk material, and this is the other difference in comparison with DSS. TSC can, in principle, study uniform bulk materials but it is limited to relatively highly insulating samples, unless cryogenic temperatures are to be resorted to. In any case, however, the interpretation of TSC data is even more dependent on the assumption of exponential trap release since there is no means of following the time dependence separately from the simultaneously varying temperature.

In sharp contrast to all these techniques, the dielectric spectroscopy of p-n junctions and Schottky diodes approaches directly the frequency-domain response of these devices under small alternating signal and under constant temperature. This method, originally called admittance spectroscopy, was appplied to Schottky diodes by Lossee [23] and by Vincent [24], the former using set frequencies and varying the temperature. Extensive studies of spectroscopy of p-n junctions were made by Loh, Charoensiri-watana and Favaron and a summary of their results is presented in reference [7]. Using wide ranges of frequency - up to six decades - and of

the height of the barrier, or gradual change of structure of the material at the barrier [18]. This interpretation links very closely the phenomena of LFD and negative capacitance.

OTHER EXPERIMENTAL TECHNIQUES

A brief mention will be made of other experimental techniques relevant to the investigation of deep levels in semiconductors and semi-insulators. Classic among them is the Thermally Stimulated Current (TSC) technique which is especially applicable to high-resistivity materials such as semi-insulators and insulators, but can be applied to semiconductors [19] . The principle of the method is to fill deep traps by optical or electric injection methods and to lower the temperature while doing so to a sufficiently low value that the trapped charges cannot be thermally released. With a biasing voltage applied to the sample the temperature is then raised in a linear ramp and the current is monitored as function of the temperature showing initially an exponential rise with $1/T$ and subsequently going through a peak at a temperature T_m . The current eventually should fall to zero except for any dark current due to the finite conductivity of the sample. The energy of the traps can be determined from the initial rise or from the loss peak temperature using certain simple assumptions about the nature of the release process. The limitation of the method arises from the dark current and from the need to cool to sufficiently low temperature to prevent re-emission, which means that shallow levels cannot be detected. Capture cross-sections cannot be determined reliably by this technique. Its principal advantage is simplicity of the equipment required for the study of TSC .

Thermally Stimulated Capacitance (TSCap) is a development of the TSC technique and its adaptation to the study of p-n junctions[20]. A junction is biased forward or reverse in order to establish a non-equilibrium population of carriers in deep trapping levels in the space charge region and the device is then cooled with the bias applied until the trapped charged become frozen in. The bias is then removed and the capacitance of the junction is monitored at some suitably high frequency while the temperature is being raised as in the TSC method. The capacitance changes as carriers are released from traps since this produces changes in the space charge density and hence in the width of the space charge region. Quantitative analysis requires the use of specific models, such as the Shockley-Read-Hall statistics [20] with its inherent assumption of exponential development of carrier release.

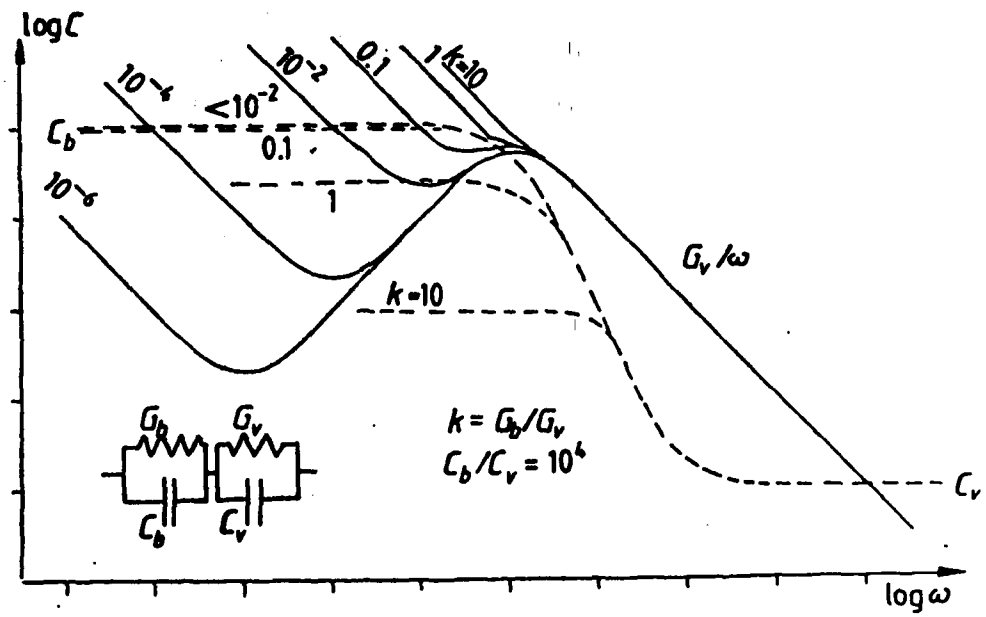

Figure 4

The frequency dependence of the effective complex capacitance components - the real part shown by dotted lines, the imaginary part by solid lines - for a series combination of two paralle G - C circuits, represening the barrier and volume regions of a semiconductor sample, denoted by the subscripts b and v, respectively. A fixed ratio of capacitances C_b/C_v was chosen and the variable parameter is the ratio of conductances $k = G_b/G_v$. The diagram shows that the loss peak disappears when the barrier conductance becomes comparable with the volume conductance. The low-frequency limit of C' is also influenced by large values of k. The high-frequency properties are independent of k being determined by the volume response. The loss peak occurs at $\omega_p = G_v/C_b$, provided that this is larger than G_b/C_v, as is likely to be the case in most situations.

over the top of the barrier, may be regarded as fast for our purposes. This results in a parallel barrier conductance G_b appearing across the barrier capacitance C_b . However, if the process of traversing the barrier in either direction is accompanied by some intermediate trapping at or near the interface, then a delay in response is inevitable and this may result in a frequency-dependent component of the complex barrier capacitance. We shall see later that such processes are in fact observed in our experiments.

The conductance of the volume of our samples is given by the volume dc conductivity σ_0 and the geometrical factor A/ω_s. The resulting series-parallel combination shown in Figure 4 has its frequency response as shown in the main diagram, on the assumption of frequency-independent ideal capacitors C_b and C_v . A loss peak arises from the interaction C_b with G_v at $\omega = G_v/C_b$, the high-frequency loss being $C'' = G_v/\omega$ while the low-frequency loss is determined by the barrier conductance $G_b = kG_v$ The larger k the less pronounced is the low-frequency side of the loss peak , until eventually for $G_b \geq G_v$ the loss peak has disappeared. It should be noted that for a given ratio C_b/C_v the low-frequency value of the saturated C' decreases as k increases.

These relations are modified only slightly if the barrier capacitance is taken to be of the dispersive type given by eqn (3) - the loss resulting from the series resistance interaction has a $1/\omega$ frequency dependence and the real part goes as $1/\omega^{n+1}$ as in eqn (14) .

We complete this introductory discussion of the various types of dielectric behaviour of barriers with a mention of the phenomenon of negative capacitance. This has been reported in a variety of contexts, usually associated with liquid and ionic systems, although one example of a partial onset of negative capacitance, resulting in a reduction of the low-frequency values of $C'(\omega)$ has been reported in amorphous silicon Schottky diodes [17]. Various interpretations have been proposed, including the highly unlikely "inductive" behaviour, and some special recombination processes [17] . We have observed very well developed negative capacitance effects which show variation with temperature and with bias and our own interpretation of this phenomenon invokes the physical significance of the corresponding time-domain behaviour. This consists of charging currents which *rise* over part of the time , instead of following a monotonically decreasing trend as in positive capacitance. There may be many causes of this rise, typical examples being double injection

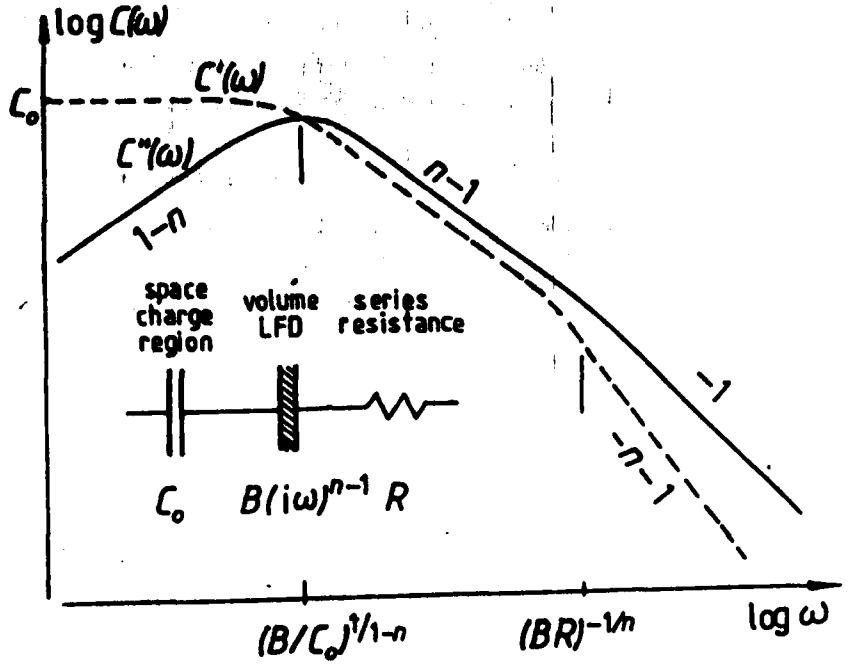

Figure 3

The dielectric response of a circuit consisting of a strongly dispersive element representing a volume LFD process without frequency limitation in series with an ideal loss-free capacitor representing a loss-free barrier region and a resistor . The characteristic frequencies for the loss peak and for the transition from the "universal" response corresponding to the dispersive element to the resistance-dominated region are indicated, as are the slopes of the logarithmic plots in the various regions. The resulting loss peak is symmetric, as for a Cole-Cole model.

an ideal loss-free capacitor C_0 . The complex capacitance of this combination is :

$$C(\omega) = \frac{C_0}{1 + (C_0/B)(i\omega)^{1-n}} \qquad (13)$$

which is exactly of the Cole-Cole form given by eqn (3) and where B replaces the pre-factor $\Delta\chi$ in eqn (4). This symmetric loss peak has frequency dependences ω^{1-n} and ω^{n-1} at frequencies respectively much lower and much higher than the loss peak frequency $\omega_p = B/C_0)^{1/1-n}$. This combination gives a high saturated barrier capacitance C_0 at low frequencies and an LFD behaviour at high frequencies.

The physical justification of this model lies in the fact that our Schottky region is by itself relatively loss-free and when it is placed in series with a bulk LFD region the predicted response of eqn (13) will be found to be exactly as seen in our experimental data, at least as regards the high-frequency response. The loss response below the peak is difficult to determine experimentally in view of the generally high barrier conductance.

These relations are represented in Figure 3 which also takes the analysis one stage further to include the effect of a series resistance R arising from the volume. The presence of the capacitor C_0 does not affect the high-frequency interaction between R and the LFD element, the combined behaviour being given by [5] :

$$C(\omega) \cong \frac{\sin(n\pi/2)}{BR^2\omega^{1+n}} - \frac{i}{\omega R} \quad , \quad \omega \gg (BR)^{-1/n} \qquad (14)$$

This gives the generally valid result that a series combination of a resistor and a dispersive element shows the real part $C' \propto \omega^{-1-n}$ while the imaginary part goes as $C'' \propto 1/\omega$, so that the logarithmic plots diverge. In no way can one obtain the universal dependence (4) by any series combination of resistors and dispersive elements.

We consider next the effect of finite dc conductance of the barrier and of the volume regions. Taking the barrier first, it is evident that all Schottky barriers are capable of transmitting some carriers from the metal to the semiconductor and vice-versa. The resulting leakage current is independent of frequency if the processes leading to its appearance may be considered to be "fast" on the time scale of the reciprocal frequencies of interest. Direct thermal excitation of carriers over the barrier, without or with a contribution from tunnelling

to a corresponding modulation of the space charge width, with a consequent displacement of the free carriers at the edge of the space charge region. The relaxation time of these carriers is $\tau_f = \varepsilon_s/\sigma_0$ and in typical materials this is of the order of nanoseconds, but in SI GaAs with $\sigma_0 = 1$ μS/m it becomes of the order of 100 μs which corresponds to a frequency of 1 kHz. At frequencies $\omega \gg 1/\tau_f$ free carriers cannot follow the variation of the space charge width and the capacitance of the system drops from the low-frequency value corresponding to the Schottky barrier $C_b = A\varepsilon_s/w_0$ to a much lower value corresponding to the geometrical capacitance of the substrate wafer at "high" frequencies $C_\infty = A\varepsilon_\infty/w_s$, where w_s is the thickness of the substrate. The loss peak frequency arising from the interaction of the barrier capacitance with the series resistance of the substrate volume is given by

$$\omega_s = G_v/C_b = (w_0/w_s)(\sigma_0/\varepsilon_s) = w_0/w_s\tau_f \ll 1/\tau_f \qquad (12)$$

In the absence of generation and trapping processes, the entire dielectric response of the barrier-substrate system would be just the Debye-like response of the series combination mentioned above. If deep traps are present in the material then the detrapping process is favoured in the plane at which the deep level crosses the Fermi level and this emission will be characterised by the expression (3) with the loss peak frequency given by the trapping emission rate ω_t. The corresponding dispersion in the real part $C'(\omega)$ usually amounts to a factor of 2 - 3 depending on the density of deep traps and we have observed this type of behaviour very clearly in Schottky diodes on extrinsic material [16] but it is completely absent from the barrier responses described in the present paper. We interpret this as evidence that the semi-insulating material on which our Schottky barriers are formed has its Fermi level pinned on the deep levels themselves, so that no emission takes place in the space charge region as such.

In principle, ordinary generation/recombination processes would be expected to contribute a similar dielectric response of their own, but in GaAs these processes have time constants in the nano-second range and would not be visible in our frequency window. We conclude, therefore, that the space charge region of our barriers may be regarded to a first approximation as a loss-free capacitor.

An important combination of "circuit elements" is given by the series connection of an LFD element characterised by the unlimited dispersive power law relation eqn (4), with no limitation in frequency, and

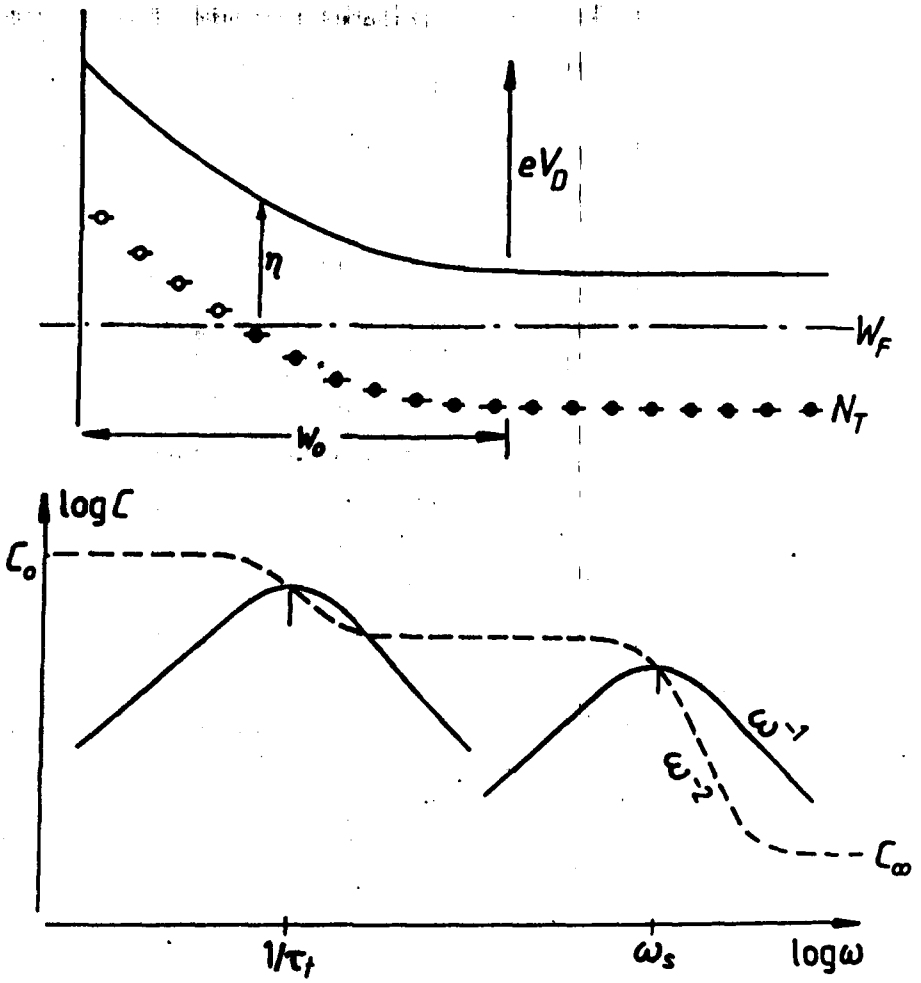

Figure 2

The band diagram - conduction band only is shown for simplicity, since the valence band does not enter into the picture - of a Schottky barrier on extrinsic n-type semiconductor. The height of the barrier is eV_D and its equilibrium thickness is ω_0 . A density N_T of deep traps is shown, but the background donor levels are omitted. The lower diagram gives the capacitance-frequency response (-----) and the corresponding loss (———) showing a small dispersion with its loss peak corresponding to the emission of electrons from traps at a frequency $1/\tau_t$ and a second large dispersion at a frequency $\omega_s = G_v/C_b$ due to the effect of the series resistance of the bulk material. The shape of the spectra is shown in the ideal situation of Debye-like responses.

mental picture. When dealing with any form of barrier phenomena it is desirable to move away from the susceptibility and permittivity notations which refer explicitly to the distributed response of a uniform medium and to express the dielectric properties in terms of effective complex capacitance $C(\omega) = C'(\omega) - iC''(\omega)$ as it is measured experimentally. For the purpose of analysis it is advisable to express the results in the form of the reduced complex capacitance

$$\tilde{C}(\omega) = [C'(\omega) - C_\infty] - i\,[C''(\omega) - G_0/\omega] \tag{9}$$

from which the high-frequency limit capacitance C_∞ and the dc term G_0/ω have been subtracted, so that $\tilde{C}(\omega)$ is the equivalent of dielectric susceptibility and its real and imaginary components are directly Kramers-Kronig-compatible (KK). The usual relationship between the permittivity and the capacitance is through the geometrical factor

$$C = A\,\varepsilon/w = (A/w)\,[\varepsilon_0\chi + \varepsilon_\infty - i\sigma_0\,\omega] \tag{10}$$

where A is the area of the sample and w the effective thickness of the relevant region. If the experimentally determined value of $C'(\omega)$ is such that assigning the actual sample thickness gives a value of ε within a factor of not more than, say, 5 ~ 10 of ε_∞, then it is reasonable to infer that the behaviour in question is due to the *volume* response of the sample. If, on the other hand, the measured low-frequency capacitance has values exceeding the C_∞ value by several orders of magnitude, then it is necessary to infer that one is dealing with a *barrier* response, since it would be completely unreasonable to assume that the permittivity of the material could be raised by the corresponding factor. This leads us to the concept of a Schottky barrier on a semiconductor in the vicinity of a metallic contact, as shown in Figure 2. The band bending of the semiconductor, assumed to be n-type, is due partly to a difference between the contact potentials of the metal and of the semiconductor and partly to the pinning of the Fermi level at the interface by a high density of surface states [14,15].

Assuming a uniform density of donors N_D and a band bending by a diffusion potential V_D the equilibrium width of the space charge region is given by the expression

$$w_0 = (2V_D\varepsilon_s/eN_D)^{\frac{1}{2}} \tag{11}$$

where ε_s is the permittivity of the semiconductor. The barrier height is lowered or increased by the application of a forward or reverse bias, respectively. The application of a small alternating signal gives rise

The third example of volume response is shown in Figure 7 referring to an undoped sample R21 F1 in which the similarity with the earlier examples lies in the high-frequency response , with $n = 0.42$ in this case, and in the coincidence between the low-frequency loss and the high -frequency loss at their cross-over with $C'(\omega)$. The difference consists in the very anomalous temperature dependence of the loss peak frequency shown in diagram b), a behaviour akin to that normally associated with a phase transition occurring in the temperature interval between 140 and 200K with very different activation energies on both sides. The details of the effect of the phase transition on the frequency spectra of $C'(\omega)$ and $C''(\omega)$ are shown in Figure 8a) and b), relating respectively to temperatures below and above 250K, giving normalisations of $C'(\omega)$ and $C''(\omega)$ with the same displacement locus. Below 250K $C'(\omega)$ shows a LFD with $n \doteq \frac{1}{2}$ but with a superimposed dc conductivity, a behaviour clearly compatible with volume dispersion over less than two decades. Between 250 and 300K there is a transition to barrier behaviour which becomes fully developed above 300K with an activation energy of 0.5 eV.

In describing this behaviour in an earlier publication [28] we have referred to it as an "electronic phase transition" since no structural transition is known to occur in this temperature range in GaAs and we are therefore dealing with some hitherto unexplored aspect of electron-phonon interactions. It is interersting to note in this connection that there are references in the literature to anomalous behaviour of SI GaAs in approximately similar temperature region. Theoretical study by Pistoulet [29] reports the effects of fluctuations in EL2 centres which might lead to a behaviour analogous to our LFD in the volume of the material. A transition in the mobility of carriers has been predicted theoretically around 140- 170K [30] and appears to correspond to the experimental findings of Walukiewicz et al [31] who find a metastability in Hall mobility , albeit at a lower temperature, in the presence of photoexcitation . An anomalous temperature dependence photo - capacitance was also reported in the range 140-170K [32]. The common theme in this is the postulated influence of EL2 centres in SI GaAs material.

Our own measurements using DSS appear thus to relate to an increasing body of experimental information, backed by some theoretical analysis, which all point in a similar direction, but it may be that our method is more sensitive in this respect than some of the steady state measurements reported.

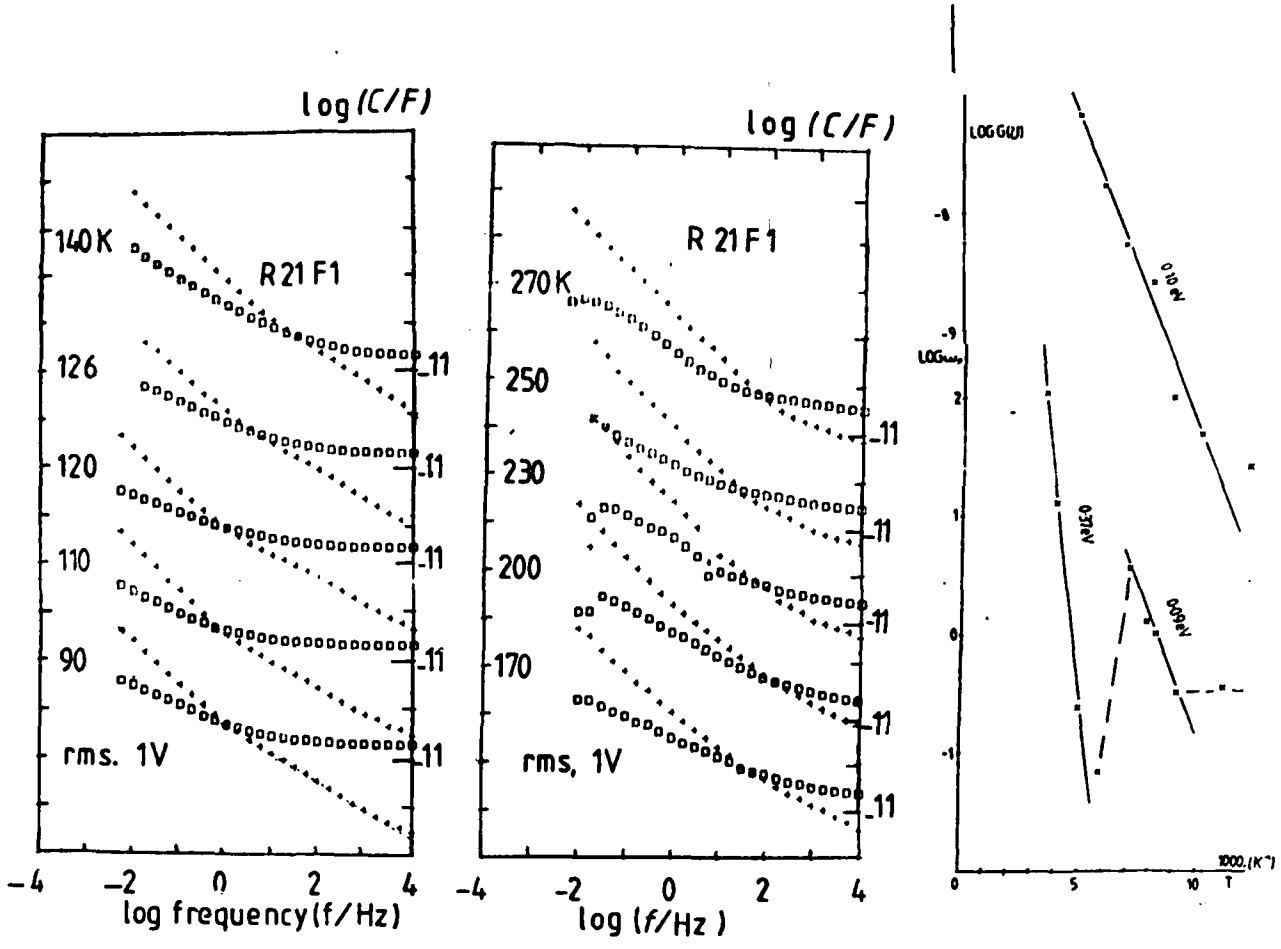

Figure 7

The dielectric response of the undoped sample of GaAs R21 F1 in the temperature range 90 - 270K. The most significant feature of these results is the anomalous temperature dependence of the frequency shift, which behaves in a manner reminiscent of a phase transformation in the temperature range 140 - 200K. The activation plot for dc conductivity does not show any anomaly.

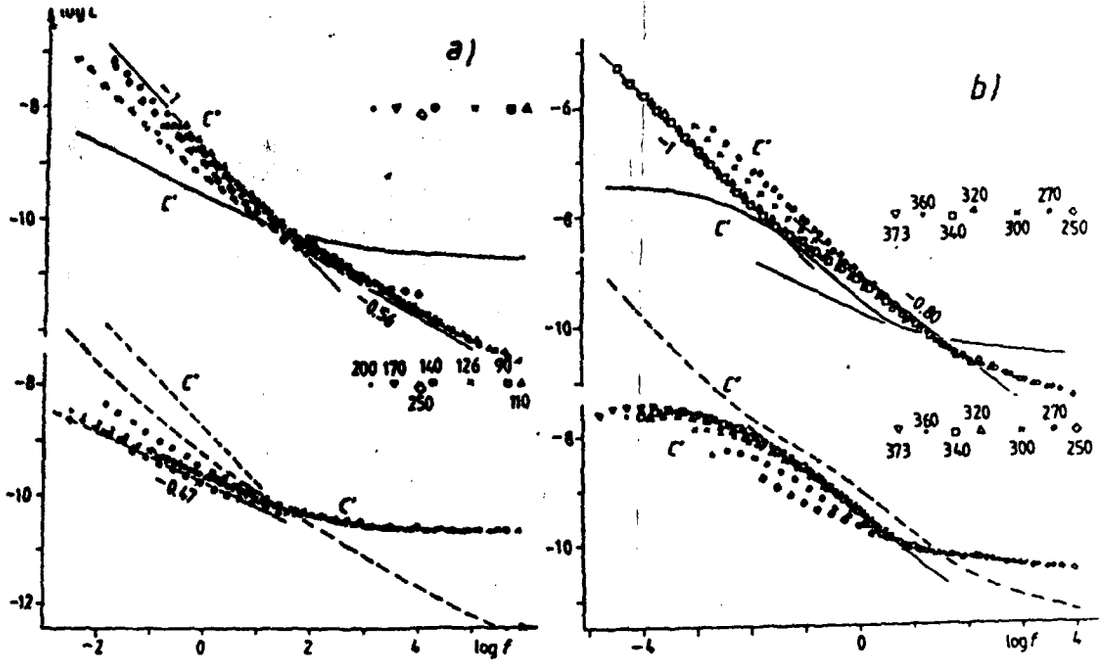

Figure 8

Normalisation of dielectric data for sample R21 F1, the same as in Figure 7, shown separately in two temperature ranges , the lower ones being clearly volume responses, those in the higher range being barrier dominated. Diagram a) for the lower temperatures shows the anomalous shift of the representative point for 250K . The solid contour on the upper loss normalisation gives the outline of the real part from the lower diagram, the dotted contours in the lower diagram for the normalisation of the real part give the outline of the loss in the upper diagram. The values of the logarithmic slopes are indicated. Diagram b) gives the corresponding representation of normalised data for the higher range of temperatures , which are not shown in Figure 7.

BARRIER DIELECTRIC BEHAVIOUR

We begin our presentation of barrier responses with Figure 9 relating to the undoped sample A333 A4 in the temperature range 300 - 360K . We note a similar behaviour of the dc contribution to loss, G_0/ω_p in relation to the onset of saturation of $C'(\omega)$ as in the volume responses , but this time in decidedly barrier context. The activation energies for the frequency shift and the dc conductivity are very close to one another, at 0.53 and 0.54 eV, respectively, and this is borne out by the almost invariant shape of the frequency response throughout the temperature range. The barrier response is near-Debye, with $n = 0.10$ in the high-frequency region. Nothing can be said of the low-frequency loss since this appears dominated by dc conductance. A more detailed analysis of the barrier response is shown in Figure 10 giving the normalisation of the reduced capacitance $\tilde{C}(\omega)$, eqn (9), confirming the K-K compatibility of the real and imaginary components.

$C'(\omega)$ shows a distinct rise at the lowest frequencies and highest temperatures, an effect which in the barrier context will be found in several other examples and which will be discussed in detail later . However, we also note the substantial saturation of $C'(\omega)$ at low frequencies , the ratio of this low-frequency value to the geometrical capacitance being approximately 2½ orders of magnitude. The entire response is near-Debye in nature and this is incompatible with the notion of a series combination of a resistance and a dispersive capacitance, as was explained earlier. At the same time, the numerical value of the series resistance required to explain the observed $\omega_p = 2.5$ at 300K together with the barrier capacitance $C_b = 10^{-8}$ F is $R_v = 1/C_b\omega_p = 4 \cdot 10^7\ \Omega$. We do not know the sample geometry with sufficient accuracy to calculate the resistivity, but we may recover this factor from the value of C_∞ on the assumption that $\varepsilon_\infty = 10^{-10}$ F/m, with $C_\infty = 10$ pF. From this the volume resistivity is obtained $\rho = R_v C_\infty/\varepsilon_\infty = 4 \cdot 10^6 \Omega m$, which is very close to the reported resistivity of this material.

The only way of reconciling this apparent contradiction, on the one hand the agreement of the resistivity with the value required for series resistance effect and , on the other hand, the inadmissibility of the series resistance response, is to assume the model proposed in Figure 3. The barrier response is , in fact ,due to the interaction of the volume LFD with the nearly loss-free capacitance of the space charge region. The series resistance effect shown in Figure 3 is absent from our data, for the simple reason that the LFD response [illegible]

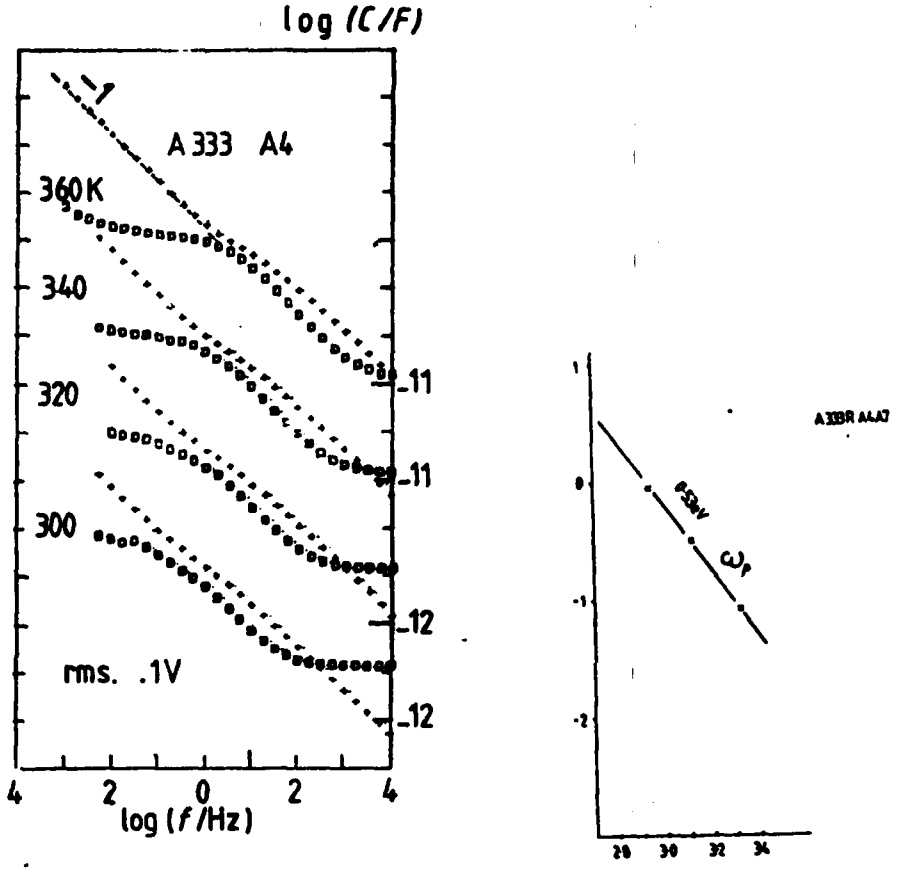

Figure 9.

The dielectric response of the sample A333A4 at four temperatures in the range 300 - 360 K , displaced with respect to one another by two decades for clarity. The high-frequency slopes of the loss (++++++) are -0.90, the low-frequency slopes are - 1 , suggesting a non-Debye character of the high-frequency response and showing that the low-frequency behaviour is due to the parallel barrier conductance G_b. The inset shows the activation diagrams for the barrier conductance and for the peak frequency ω_p. The real part $C'(\omega)$ (□□□□□□□) shows an almost plateau region at lower frequencies, defining the barrier capacitance $C_b(0)$, with a clear ten dency to a further rise at the highest tempeatures. The high-frequency value corresponds well the geometrical capacitance of the sample.

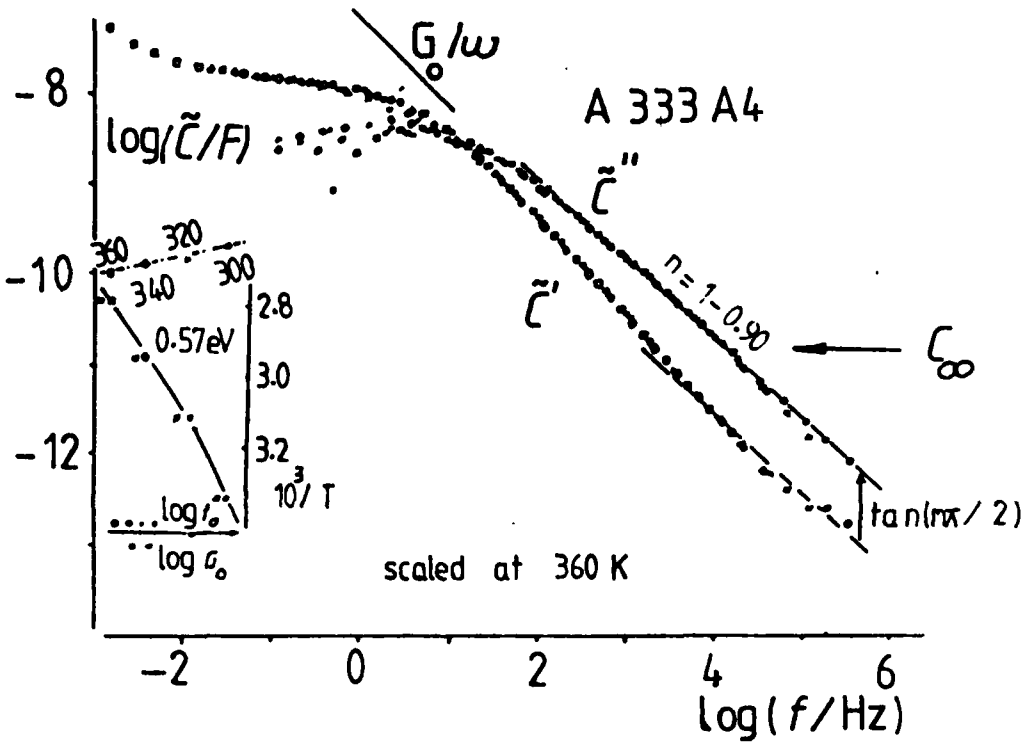

Figure 10

Normalisation of the data for the sample shown in Figure 9 in the form of the reduced capacitance $\tilde{C}(\omega)$ defined by eqn (8). The non-Debye character of the response at frequencies above the loss peak is evident and the Kramers-Kronig compatibility of the data is shown by the two parallel lines. The insets show the activation energies for the frequency shift and for the dc conductance G_b The slight discrepancy between the activation energies in Figure 9 and here is due to the fact that the normalisation here was carried out "manually", while the activation plots in Figure 9 were obtained from computer fitting of data.

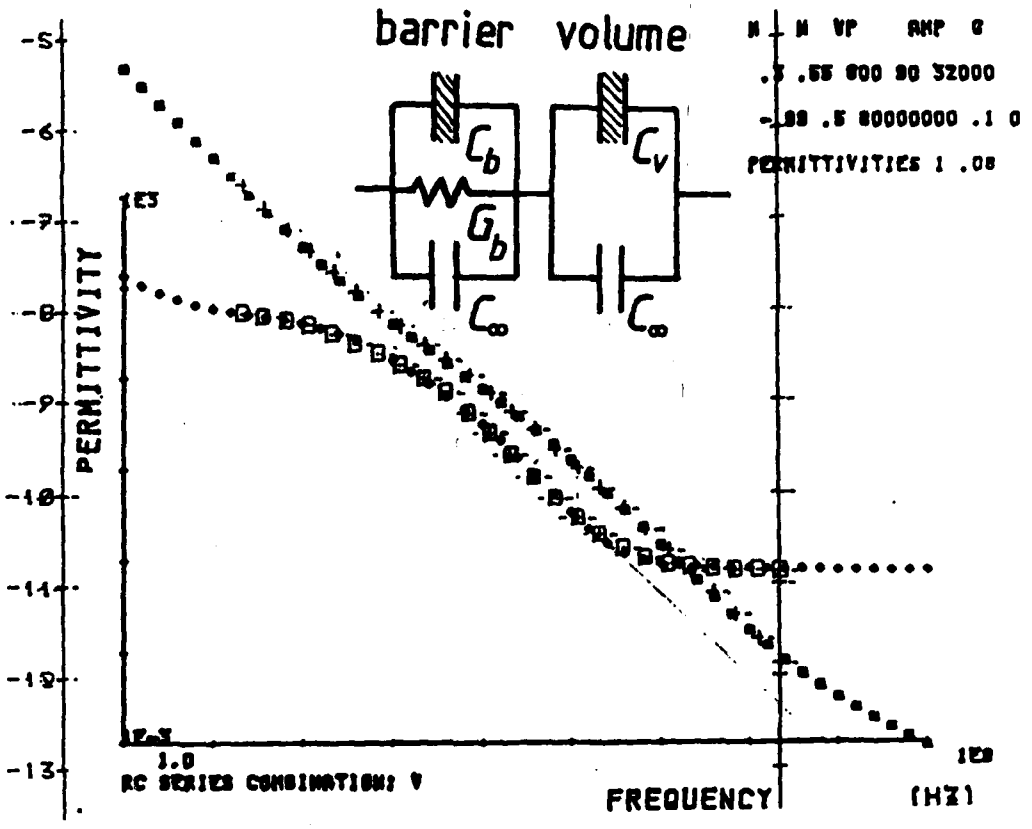

Figure 11

Computer fitting of model circuit response to the experimental data for sample A333 shown in Figure 9 at 300K . The elements of the assumed circuit are shown in the inset and they consist of a volume element in which an LFD response is in parallel with a suitable C_∞ , and this is in series with a barrier element characterised by a loss peak with high-frequency slope of 0.45 in parallel with a conductance.
Measured points □□□□ and ++++ , computed points ♦♦♦♦ and ■■■■ .

so nothing else can appear in series. The loss peak frequency is given by $\omega_p = (B/C_0)^{1/1-n} \cong B/C_0$ since n is small , and the parameter B corresponds closely to the quasi-dc conductivity of the volume of the material, which explains the agreement with the series resistance expectation. This discussion emphasises the problems which are liable to arise in the determination of dc conductivity of SI GaAs , where a "static" measurement may not necessarily reveal the true state of affairs in the presence of LFD .

The result of computer fitting of barrier and volume parameters is shown in Figure 11 for the 300K data. A good agreement between the measured and fitted data is obtained over the entire frequency range of six decades. This technique is particularly valuable when evaluating the temperature dependence of different components of more complex spectra.

The behaviour of the same Cr-doped sample "B" as in Figure 5 in the higher range of temperatures is shown in Figure 12 which reveals a number of interesting features, some of them similar to those seen in Figures 9 and 10. This sample shows clearly a slight dispersion in the volume at the level close to the geometrical capacitance C_∞ and recognisable already at the lower temperatures in Figure 5. The dc conductivity of the volume material, resulting in the -1 slope at low frequencies, is characterised by the same relation as was found earlier, $G_v \cong \omega_p C_\infty$ and the volume process has the post-peak exponent $n = 0.4$. At around 300 K the volume conductivity becomes replaced by a loss process with a slope distinctly smaller than -1 , reminiscent of LFD, while the $C'(\omega)$ curve tends to saturation. It becomes evident, however, that this saturation goes over into negative capacitance at still higher temperatures and the change of sign occurs at progressively higher frequencies.

The evaluation, as near as it is possible, of the "dc conductivity" as function of temperature shows a strongly non-Arrhenius shape of the activation plot, which gives a continuous curvature from approximately 0.6 eV at the highest temperatures to the values of around 0.07 eV at the lowest temperatures as seen in Figure 5.

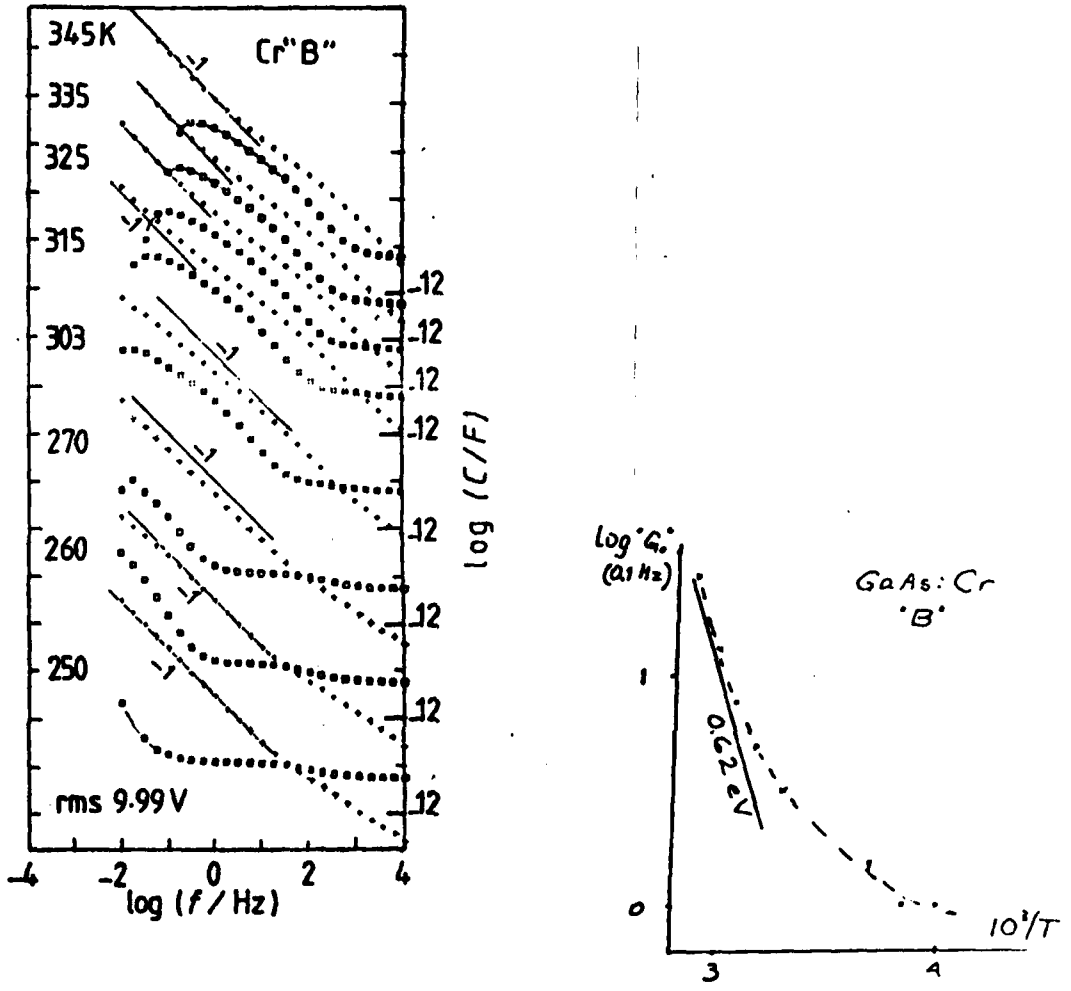

Figure 12

The dielectric spectra for the same sample Cr-B as shown in Figure 5 but corresponding to higher temperatures. Slopes of -1 are drawn where appropriate to indicate the regions dominated by dc conductance in the barrier . Note the slight volume dispersion with its loss component of high-frequency slope - 0.6 and a gradual evolution of LFD which eventually becomes superseded by a tendency to negative capacitance. The activation energy of dc conductivity in the barrier at 0.1 Hz is shown in the inset, tending to 0.6 eV at high temperatures and tailing off to much lower values consistent with the value of 0.07 eV found at low temperatures in Figure 5.

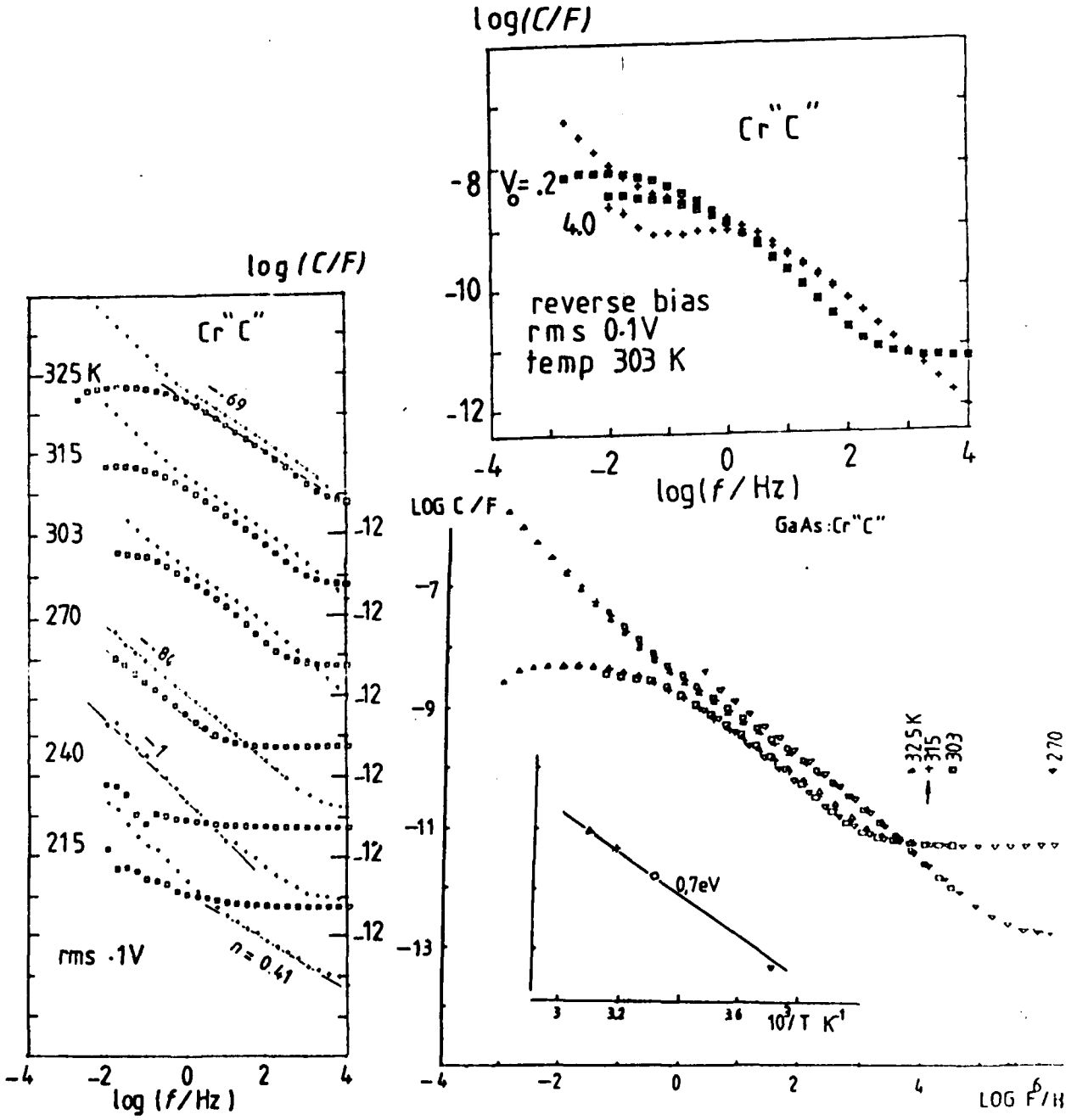

Figure 13

The response of a Cr-doped sample Cr-C over a range of temperatures 215 - 325K , showing a gradual evolution of a complex barrier behaviour with an activation energy of 0.7 eV at higher temperatures. The lower temperature data are not normalisable with the higher temperature ones, showing an incipient LFD with dc conductivity in parallel, but then going over into well defined LFD at 270K which must be regarded as volume LFD with barrier capacitance. The effect of reverse bias is shown for 0.2 and 4.0 V. Normalisation for higher temperatures is also shown.

A further example of a gradual transition from volume to barrier response is shown in Figure 13 for a Cr-doped sample labelled Cr-C. At 215 and 240 K the incipient dispersion in $C'(\omega)$ is dominated by dc conductivity at low frequencies, while the volume loss has a markedly lower slope. At 270K this is replaced by a clear-cut LFD with $n = 0.16$ and at 303K an above there is evident saturation of $C'(\omega)$ eventually giving way to negative capacitance. The two lowest temperatures are not normalisable with the remainder, as may be seen , and the activation energy for the high-temperature frequency shift is 0.7 eV . The effect of negative bias of 0.2 and 4V is also shown and it is interesting to note that at 0.2V the saturated capacitance is higher than with zero bias, while the 4V data fall at a lower level, as might be expected. Bias has no effect on the high-frequency volume behaviour, as might be expected, while it reduces the dc conductance of the barrier emphasising the loss peak.

An extensive series of measurements over a range of temperatures and also with variable forward and reverse bias and signal amplitude was carried out on an undoped sample Cominco 126 S73 which has one contact believed to be "ohmic" having been implanted on one side with $10^{15}/cm^2$ of Phosphorus ions of 170 kV energy, with Ag paint over it. The other contact is Ag paint on untreated GaAs. Figure 14 b) gives the temperature data with zero bias at 0.1 V rms signal. LFD appears below 240K with a gradual onset of saturation of $C'(\omega)$ at just over three decades above C_∞ . There is no sign of any tendency to negative capacitance. The conductance of the barrier is comparable to the volume conductance giving the characteristic relative positions of loss and $C'(\omega)$near the saturation point, in accordance with Figure 4.

The corresponding data with a forward bias of 0.2 V are shown in diagram a) where there are distinct differences in comparison with diagram b). The barrier conductance is significantly higher , as may be seen from the corresponding positions of $C'(\omega)$ and $C''(\omega)$. There are variations in the frequency dependence of $C'(\omega)$, with a marked tendency to a slope of $-\frac{1}{2}$ and, at higher temperatures, to negative capacitance. It is evident, therefore, that the dynamics of barrier transport is markedly affected by even the relatively small value of forward bias.

By contrast, a reverse bias of 3 V brings about a reduction of barrier conductance , resulting in the appearance of the loss peak, and there is also a reduction of the value of the saturated C' at low frequencies, diagram c).

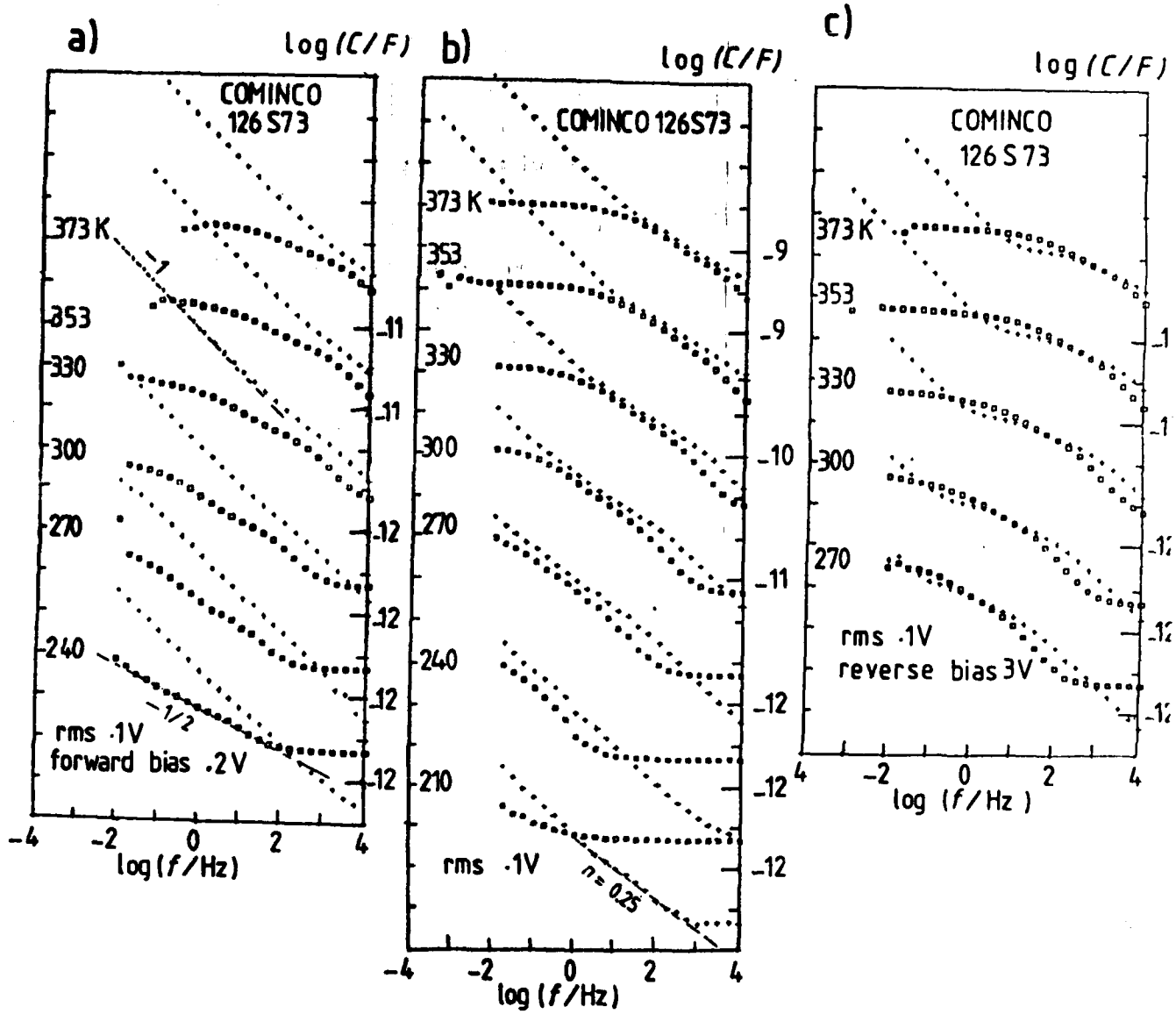

Figure 14

The dielectric response of a sample of undoped GaAs Cominco 126 S73 with variable temperature and with zero bias, diagram b), forward bias of 0.2 V , a), and reverse bias of 3 V, diagram c). Representative values of slopes are indicated .

The normalisation of the zero-bias data is shown in Figure 15 for the temperatures from 210K upwards. The LFD region in the volume of the material has a very small value of n in its higher-frequency region, as well as being characterised by a complex structure with a much smaller value of slope. This sample, in common with many others, shows a low inherent loss at high frequencies , corresponding to a value of $\tan\delta \simeq 0.01$ which appears to be independent of frequency.

The effects of variable bias and amplitude of the alternating signal are shown in Figure 16. Diagram a) gives the effect of increasing forward bias, the upper part giving the separate plots for various biases, the lower part giving the presentation of all the results on common ordinate scale. It is clear that forward bias has no effect on the high frequency part of the characteristic, in common with our earlier findings. The low-frequency part of the response shows an increase of barrier conductance, which is understandable, but at the same time a decrease of real part $C'(\omega)$ which is contrary to classical expectations, but which may be understood in terms of progressively increasing tendency to negative values of capacitance. Reverse bias has relatively little effect on the dielectric spectrum, apart from initially reducing the dc conductance of the barrier an ultimately increasing it again beyond 3V bias, suggesting that the barrier is "soft" , diagram b).

The effect of increasing amplitude of the rms signal , diagram c), is somewhat similar to the forward bias which may be understood in terms of the generator being dc coupled to the device, so that increasing amplitude effectively increases the forward component of the current proportionally more than the reverse component.

Figures 14 and 16 show the complex nature of the various processes governing the dielectric response of interfacial phenomena - their strong dependence on the value of the bias and of the amplitude and their temperature dependence which brings out progressive changes in the spectral shape of the response , and not just a progressive shift of the spectrum in frequency. It is difficult, on the basis of the information at our disposal, to give a definitive opinion on the model which represents the situation most probably - whether we are dealing with a bulk LFD interacting with a barrier capacitor, as in Figure 4, or whether there is a series interaction of barrier process of near D.C. character with the volume conductance . This question has to remain unanswered for the time being, although in some other cases the balance of probability is in favour of the first possibility.

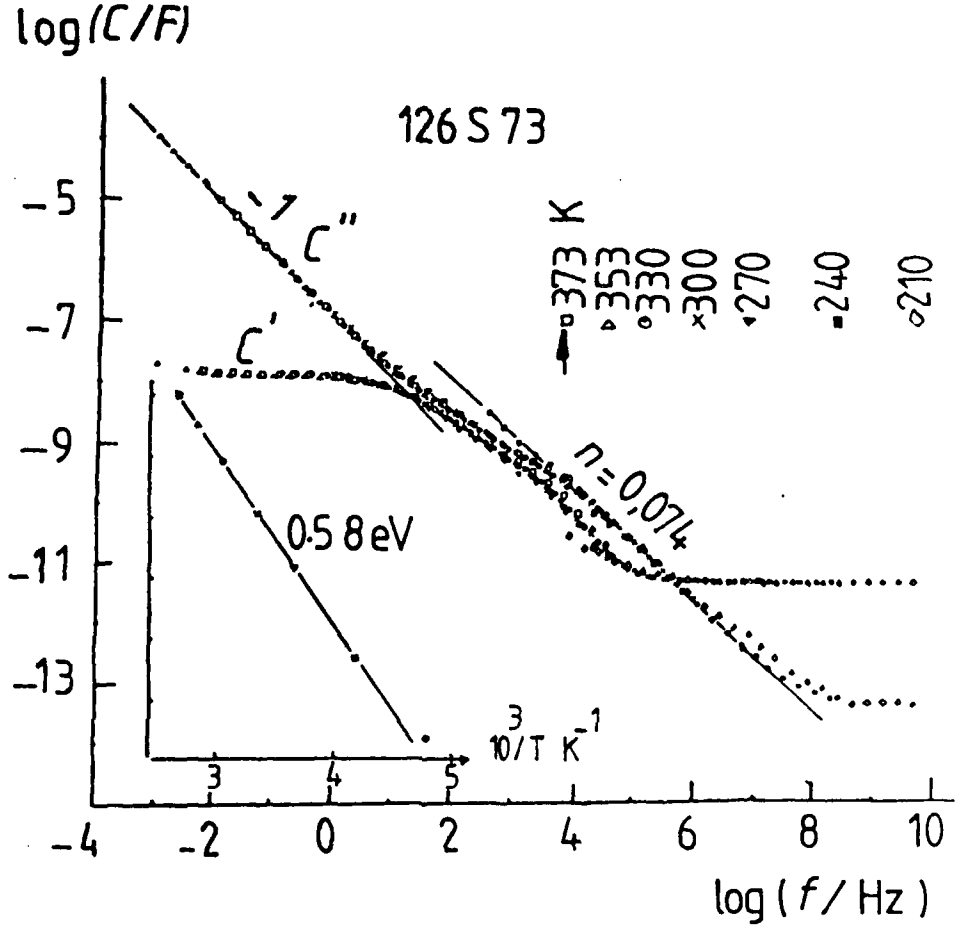

Figure 15

Normalisation of data for the range of temperatures in diagram 14 b) together with the relevant activation plot showing a single activation energy of 0.58 eV in the temperature interval shown. There is some mismatch in the central part of the response since the shape of the spectra is changing continuously.

However, the general shape of the master curve comes out clearly and reveals the complex nature of the dispersive region.

INTRODUCTION

Schottky diodes represent one of the earliest types of semiconductor devices whose theoretical understanding ought to be regarded as well-established and which should present few experimental surprises. The particular investigation reported here of the dielectric response of Schottky diodes on n-type GaAs has revealed a number of features which were not expected and which can only imperfectly be accounted for on the basis of our present knowledge of this material. Our experimental results open up a number of fundamental questions relating to the interfacial processes on GaAs and it is evident that novel concepts have to be developed to achieve a proper understanding of the experimental data which are well-established and present no doubt with regard to their validity.

The technique of dielectric spectroscopy of semiconductors (DSS) is described in detail in the accompanying report referred to as I, and it will be sufficient to state that it measures the complex capacitance of a Schottky diode over a wide range of frequencies between 10^{-2} and 10^{4} Hz, and over a range of temperatures, with external steady bias and with the amplitude of the applied alternating signal as additional parameters. The technique measures essentially delayed transitions in the system under investigation, in the present instance primarily the emission and capture of charge carriers - electrons in the case of n-type semiconductors - in deep levels near the interface. There are also important contributions to the response from interfacial reactions, some of which are clearly of an electrochemical nature and suggest the presence of certain instabilities in the devices under study.

While Schottky barriers were present in many of the wafers of semi-insulating GaAs described in I, their response was always intermingled with the behaviour dictated by the delayed transitions in the bulk material. By contrast, the behaviour of Schottky diodes on n-type material referred to in the present report, is essentially dominated by barrier phenomena, the resistivity of the bulk material being too low to give rise to series $R - C$ effects and to a fine structure arising from bulk phenomena. To that extent, therefore, the behaviour

PART II

DIELECTRIC SPECTROSCOPY OF SCHOTTKY DIODES ON N-TYPE GaAs

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ABSTRACT

Measurements are reported of the dielectric response in the frequency range 10^{-2} - 10^{4} Hz of Schottky diodes on n-type GaAs with aluminium metallisation, with the results revealing several important deviations from the classically expected response. The most important and unexpected phenomena are the appearance of low-frequency dispersion (LFD) and of negative capacitance, which are strongly influenced by even small (0.1V) negative and positive biases, respectively. Both phenomena are linked with interfacial processes involving some form of instability arising from structural transformations at the metal-semiconductor interface. Direct evidence of slow recovery over many hours after strong biasing supports this view. Time-domain measurements are reported in the range 10^{-4} - 10^{5}s, showing that the charging current under step-function forward biasing is *rising* over a certain time interval, while the reverse bias gives a continuously falling current. These observations are fully consistent with the appearance of negative capacitance and LFD. The steady state voltage-current characteristics also show very unusual behaviour which is inconsistent with the classical model of Schottky diodes. The conclusion is that the behaviour of Schottky diodes on GaAs is completely inconsistent with the normally accepted theories and requires a fresh approach to its interpretation.

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The spectral distinction between various horizontal and vertical transition processes provides a powerful means of establishing their nature in conditions where conventional techniques would not be able to do so. A case in point is the difference between dc conductivity and volume LFD, which would be missed by ordinary steady state measurements .

The observation in single crystal SI GaAs of volume LFD processes constitutes an important step in advancing our understanding of this unique material. Equally important is the clear distinction between volume and interfacial LFD , which show similar dielectric signatures despite the very different physical basis of their operation. The interfacial LFD process is, in turn, closely related to the phenomenon of negative capacitance, observed by us for the first time in single crystal semiconductors. The physical difference between these two consists in the fact that LFD is associated with a very slowly monotonically decreasing charging current and one that is rising over part of the time range. We expect to be able to understand the reasons for this difference and to relate them to the detailed structure of the interface. However, it is important to bear in mind that these experimental facts have only just recently become available, prior to that no one has even suspected their existence.

An important feature of our experimental technique is its ability to analyse a number of volume transition processes with low activation energies which would not be accessible to conventional DLTS techniques.

At this stage we have not attempted direct correlation between our dielectric spectra and specific defects in SI GaAs . One reason for this is the sheer multiplicity of these defects believed to be identifiable [33.34] and therefore the need for very carefully dsigned experimental work for which we have not had time so far. We regarded it as more important to establish the general pattern of dielectric responses in SI GaAs and to outline the experimental and interpretational principles od DSS as a unique technique.

As the significance of the experimental material gathered by the present work becomes properly appreciated , especially in relation to the non-exponential time dependence , so we may expect theoretical studies to be undertaken to interpret the causes of this unexpected behaviour.

ACKNOWLEDGEMENT

We wish to acknowledge the sponsorship of our work on Dielectric Spectroscopy of Semiconductors by the US Army through their European Office, including a bursary for CF. SZ acknowledges a bursary from the Government of Libya.

On the other hand, there is no comparable explanation available for the volume behaviour and this remains at present an unresolved question.

There is a further interesting feature of many of our barrier results, consisting in the appearance at higher frequencies of a region of divergent slopes of $C'(\omega)$ and $C''(\omega)$ following a region of parallel slopes consistent with near-Debye behaviour. The parallel slopes obeying eqn (5) were shown in the Introduction to be incompatible with series resistance effects and for this reason we have introduced the concept of series capacitance in conjunction with volume LFD. However, this seemed to preclude the appearance of a series *resistor* leading to the characteristic frequency dependence shown in Figure 3 and given by eqn (14) , while in our results, e.g. in Figure 14 , there appears the characteristic response shown in Figure 3. Once again, it is not clear at the present time what the explanation of this should be. In the compilation of results given in Table I these cases are referred to as "Series resistance effects".

Table I gives the summary of experimental results with the indications regarding the probable interpretations and with some of the critical parameter values.

CONCLUSIONS

The extensive study of the dielectric properties of SI GaAs presented in this paper enables us to gain a new insight into the various delayed transition processes between deep levels in semiconductors, with particular emphasis on what we believe to be the unique features of SI GaAs.

The ability to resolve the frequency dependence of the complex susceptibility over six decades , coupled with the availability of a wide range of temperatures, has provided us with experimental material relating to the dynamic response of slow transitions which is quite unique of its kind and is not available from any other experimental techniques.

It shows conclusively the non-exponential time dependence of electronic transition processes, contrary to widely held belief. The observed fractional power law in time and in frequency reveals the dependence of the exponent n on the nature of the material and also on the type of transition.

TABLE I .

SUMMARY OF DIELECTRIC RESPONSES OF SAMPLES

Fig. N°	Sample	Temp're range K	Contacts	Area/ Thickness mm^2/mm	Suggested Mechanisms	Parameters	Activ'n Energy eV	Comments
5	Cr-B	125-240	Painted Ag	20 0.42	Volume detrapping Volume LFD	$\Delta C = C_\infty$ $n = 0.36$	0.37-0.08	
12		250-335			Volume LFD + series barrier Negative capacitance	$C_b/C_\infty \sim 10^3$	= 0.6	Series resistance effects discernible
6	Cominco 160 S	183-263	Painted Ag	- 0.5	Volume detrapping and volume LFD	$n = 0.38$ $n \geq 0.1$	0.21 - 0.23	Both processes have the same energy
17		295-353			Volume LFD + series barrier Negative capacitance	$C_b/C_\infty = 10^3$	0.6-0.7	Complex spectral shape Anomalous temperature dependence of cross-over frequency.
7	R21 F1	90-250	Evapor. In	78 0.5	Volume detrapping Volume LFD	$n = 0.44$ $n = 0.5$	0.1-0.37	Electronic phase transition 140-200K.
8		250-373			Volume LFD + series barrier	$C_b/C_\infty = 10^{2.5}$	0.8	Gradual transition to barrier response
9	A333	300-360	Evapor. Al	78.5 0.1	Volume LFD + series barrier	$C_b/C_\infty = 10^{2.5}$ $n = 0.1$	0.53 - 0.57	
10					Interfacial LFD incipient at high temperatures			
13	Cr-C	215-325	Painted Ag	20 0.45	Volume detrapping Volume LFD with temperature-dependent n + series barrier Negative capacitance	$n = 0.4$	0.7	Series resistance effect becomes apparent
14	Cominco 126 S73	210 - 373	Painted Ag over ion implant on one side, painted Ag other side	20 0.45	Volume detrapping	$n = 0.25$	0.58	Series resistance effect becomes apparent
15					Volume LFD + series barrier			
16					Negative capacitance			Strong bias dependence of volume LFD
18	R34 9F	300-383	Evapor. In	78.5 0.5	Volume LFD + series barrier	$C_b/C_\infty = 10^{2.5}$	0.6-0.69	
					Interfacial LFD			Interfacial LFD disappears between 370 and 383 K.

Finally, the third process giving strong LFD is the interfacial generation/recombination which has many counterparts in other solid-solid and solid-liquid interfaces. The characteristic features of both the interfacial and the volume LFD are the absence of any definite "termination" at the lower end of the frequency range, which distinguishes these processes from the "dipolar" processes.

SI GaAs is the first material in which a well established volume LFD process has been observed over sufficiently extended ranges of frequency to be credible. In our experimental situation we have to assume that the loss peak and the saturation of $C'(\omega)$ which we associate with the barrier are, in fact, arising from a series combination of this LFD in the volume and the barrier capacitance . There is no reason, in principle why detrapping of carriers in the space charge region should not give the same type of response, but the objection in the present case is that this would almost inevitably run into difficulties with the series resistance of the volume material. In many of our examples there is no evidence of such series resistance effects, but there are a few where one might discern such influence - e.g. Figure 14.

Since LFD is a "dc-related process", it is understandable that any attempt to measure the "dc conductivity" of a material by conventional steady-state techniques must come up with a very similar answer, even though no conventional method would lead one to suspect that large amounts of charge were being stored in the system at the same time. The further question of any correlation between LFD and interfacial or volume electrochemical processes [10,11] cannot yet be resolved at the present time.

One very general feature of the dielectric responses is evident in all cases described in the present paper, *viz.* the relation between the low-frequency loss contribution of the dc conductance, G_0/ω_p at the loss peak frequency and the real part of the capacitance $C'(\omega_p)$. These two are approximately equal, within an order of magnitude, both in barrier responses and in the case of volume detrapping processes, being slightly influenced by external bias in barriers, but otherwise showing a remarkable consistency of behaviour. In the case of barriers, the implication of Figure 4 is that the barrier conductance is comparable with the volume conductance, which is a very reasonable condition, given the likely high leakage of the very imperfect Schottky barriers on SI GaAs, as distinct from the diodes made on extrinsic material.

DISCUSSION OF RESULTS

This study of the dielectric response of SI GaAs provides a good illustration of the potential of DSS as a technique for the determination of the laws governing the various rate processes taking place in semiconductors. This is made possible thanks to the very wide frequency range available and also to the considerable sensitivity of the method.

One of the principal conclusions from this study is the absence of Debye-like responses in all situations investigated by us, contrary to widely held expectations based on currently accepted models of trapping processes. Being able to establish, for the first time to our knowledge, the systematic deviations from the Debye frequency dependence, or the corresponding exponential dependence on time, should provide a good inducement to theoretical workers to develop the required background framework of rate processes involved in deep trap reactions in solids. It is to be expected that the development of such theoretical models, for which there has been until recently no experimental justification, will advance our understanding of many-body processes in condensed matter.

It is interesting and very likely significant that three very different loss processes should follow power-law frequency dependence with very small exponents n . The volume loss peak contributing a real part increment ΔC_0 comparable to C_∞ is evidently dipolar in origin, in the sense of being caused by electronic or ionic charges hopping between two preferred sites, with activation energies below 0.1 eV . We do not know at present with certainty whether the same processes can also lead to extended hopping , with its very different power law with values of n not far from unity, but the balance of probability lies in favour of this being a separate process, in view of the very clear near-Debye character which would not be compatible with multiple hops. One of the characteristic features of the "dipolar" hopping processes is the saturation of $C'(\omega)$ below the loss peak frequency .

The second process giving a similar strongly dispersive power law in frequency is the LFD in the volume of the sample which is closely related to dc conductivity but which involved the storage of very large amounts of charge in the system. It is difficult to be sure how exactly this process should be present in such apparently well ordered crystalline material as GaAs , but there are indirect indications linking it with the presence of EL2 defects which are believed to be non-uniformly distributed in the material.

The behaviour of a Cominco ingot 160S is shown in Figure 17 , referring to a sample with two painted Ag contacts without any implant damage. The most striking feature here is the strong presence of negative capacitance at all temperatures from 295K onwards, with the steeper than -1 slope of loss, consistent with this feature. It is interesting , however, to note the anomaly of the onset of negative $C'(\omega)$ in frequency between 295 and 303 K and higher temperatures. This may be yet another example of anomalous temperature responses in various contexts in SI GaAs. This anomaly of negative capacitance is accompanied by a marked decrease of G_b at 303 and higher temperatures relative to 295K , as is evident from the relative positions of $C'(\omega)$ and $C''(\omega)$.

Our last example of barrier-dominated dielectric behaviour is shown in Figure 18 and refers to an undoped Rockwell sample R34 9F . This shows broadly similar features as the previously discussed samples with the same relative change of $C'(\omega)$ and $C''(\omega)$ between the lowest temperature and the higher ones. There is also a very clearly developed tendency to a further dispersion of $C'(\omega)$ at the lowest frequencies which becomes visible at 320K and is well developed at 360 and 370K, and apparently vanishes at 387K . This behaviour is barely visible in Figures 9 and 14 and it is therefore interesting to note its presence here.

The significance of this response lies in the fact that it occurs superimposed on the *barrier capacitance* , implying a parallel process in the barrier which is not the dc conductance. We tend to interpret this as a further LFD in the barrier arising very likely from the presence of some interfacial oxide film between the metal and the SI GaAs. This interpretation is supported by the results obtainable with Schottky diodes on extrinsic GaAs in which very strong LFD phenomena are observable with a reverse bias applied to the diode [16].

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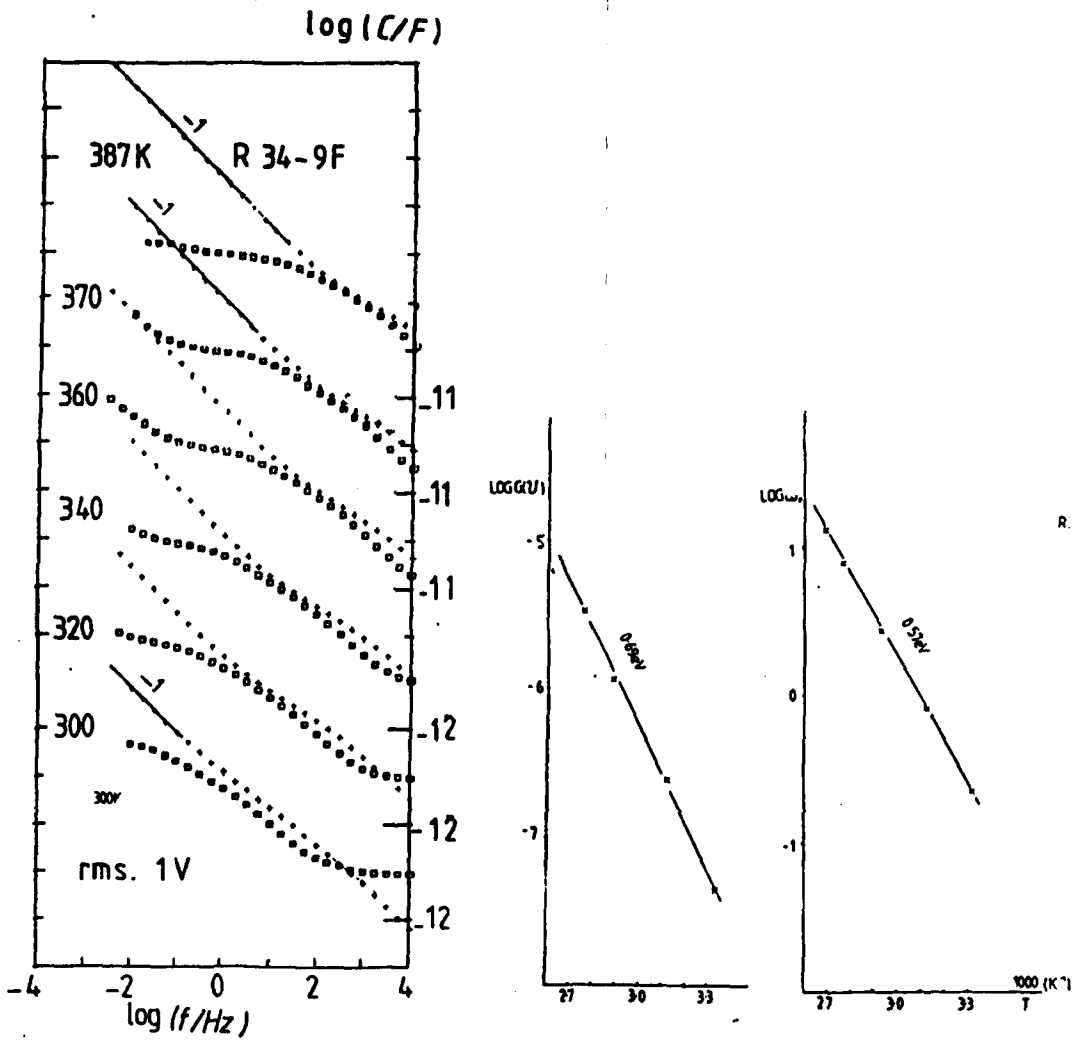

Figure 18

The temperature dependence of the dielectric response of undoped SI GaAs from Rockwell , R34 9F which is remarkable by the clear tendency to a second strongly dispersive region at the lowest frequencies which may be interpreted as an interfacial LFD.

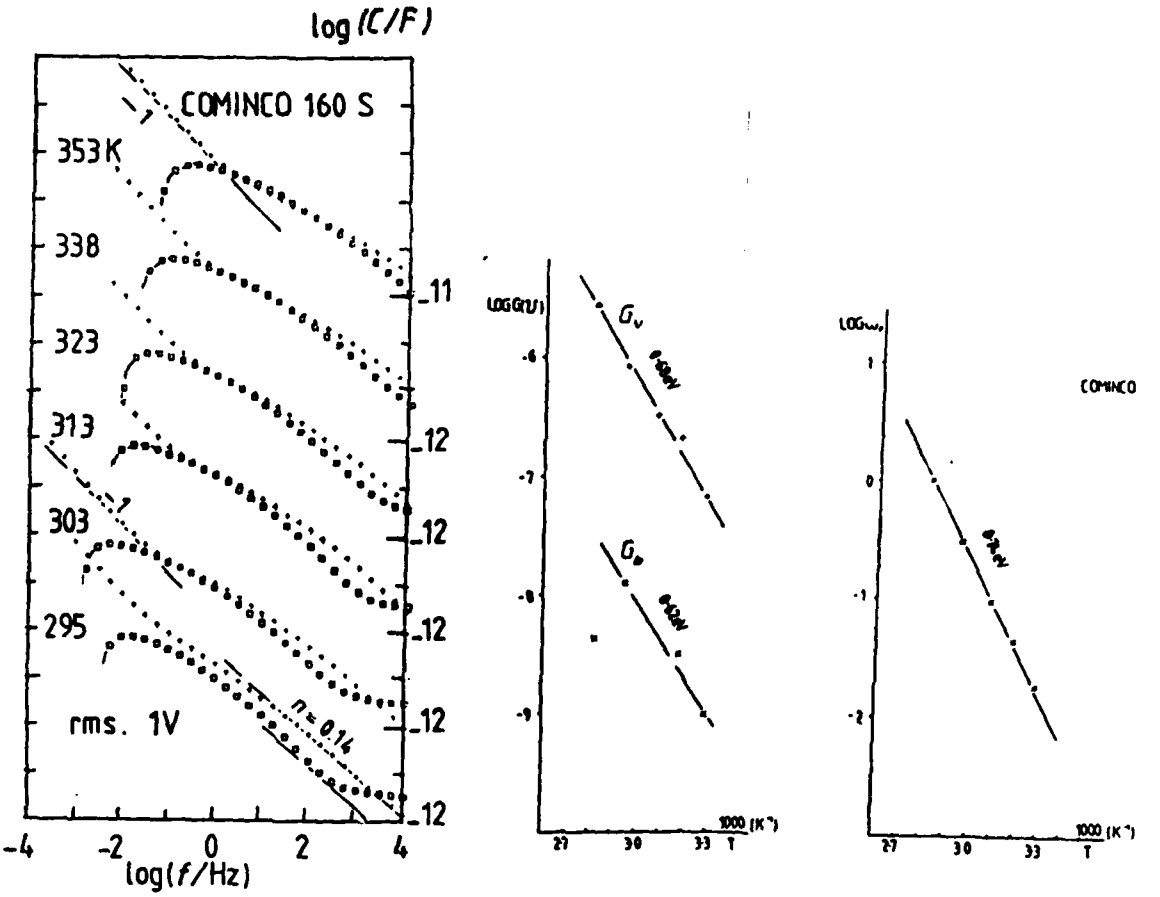

Figure 17

The dielectric response of an undoped Cominco 160 S sample with two painted Ag electrodes, showing very pronounced transition to negative capacitance at low frequencies. The transition frequency shows an anomalous temperature dependence between 295 and 303K .

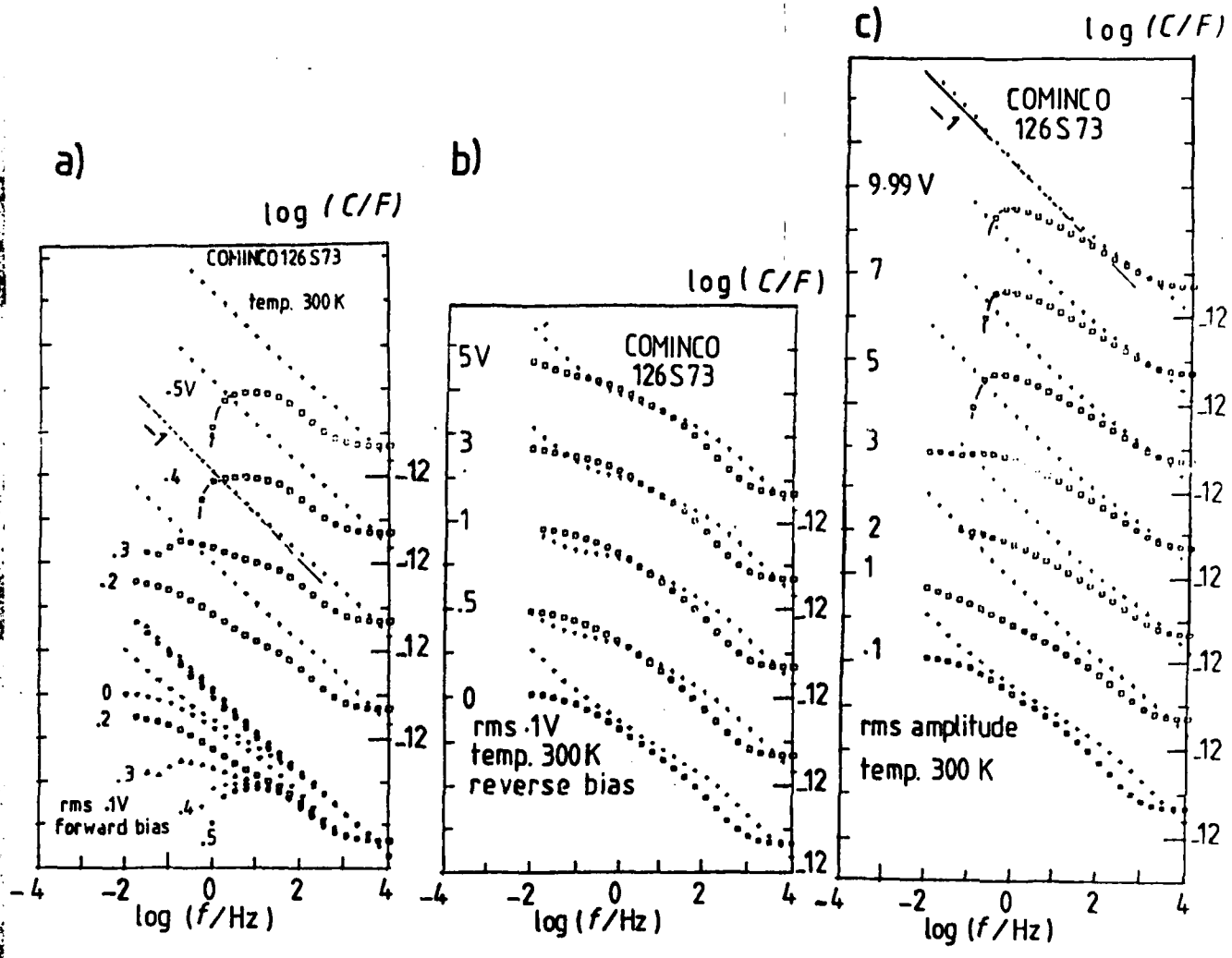

Figure 16

The bias and signal amplitude dependence of the dielectric response of the same sample of Cominco 126 S73 material as shown in Figures 14 and 15 . Diagram a) refers to increasing forward bias, diagram b) to reverse bias and diagram c) to increasing signal amplitude, all at 300 K. The lower part of diagram a) gives the presentation of bias data, including zero bias, on a common ordinate scale to bring out the rapid changes of $C'(\omega)$ leading to negative capacitance at higher forward biases. Note the steeper than -1 slope of locc points in diagram c) at 10 V amplitude, consistent with the negative capacitance values.

ought to be simpler, but as will be seen, this is not necessarily the case.

The energy band diagram of a Schottky diode on n-type semiconductors is shown schematically in Figure 1 where the shallow donors with a density N_D are not shown and where a single deep level of traps of density N_T is assumed at an energy η below the conduction band. The interfacial barrier arises as a result of a mismatch of the Fermi levels in the bulk material and in the metal, leading to a contact potential difference (CPD), which may also be due in some measure to a high density of interfacial states. For our present purpose it is immaterial which of these fundamental mechanisms is the dominant one. The equilibrium barrier height is eV_D and this quantity may be expected to depend on the temperature through the position of the Fermi level in the forbidden gap, V_D decreasing as T increases. An external bias V, reckoned positive in the forward direction, i.e. semiconductor negative with respect to the metal, is subtracted from V_D in determining the actual barrier height.

The traps below the Fermi level are fully occupied and negatively charged, empty traps above the Fermi level are neutral, resembling in this respect acceptor levels and compensating the prevailing donors. In our case we assume that $N_D > N_T$, since otherwise the material would be semi-insulating with the Fermi level lying deep at the trapping states, leading to a situation described in I.

The two shaded areas in the diagram of Figure 1b) refer to the changes of charge in the barrier region under the influence of a small-signal voltage ΔV superimposed on any steady bias. The free charge response is rapid, since the relaxation time ε/σ, where ε is the permittivity and σ the conductivity, is typically in the nanosecond range and below. The deep traps respond much more slowly and the delayed response gives rise to the observed behaviour of the barrier region at sufficiently low frequencies, where the shift of the occupied populations of the free and trapped charges is the same and equal to Δw_s, the subscript referring to "slow" responses. At sufficiently high frequencies, on the other hand, the only charge movements are in the free carriers at the edge of the space charge region.

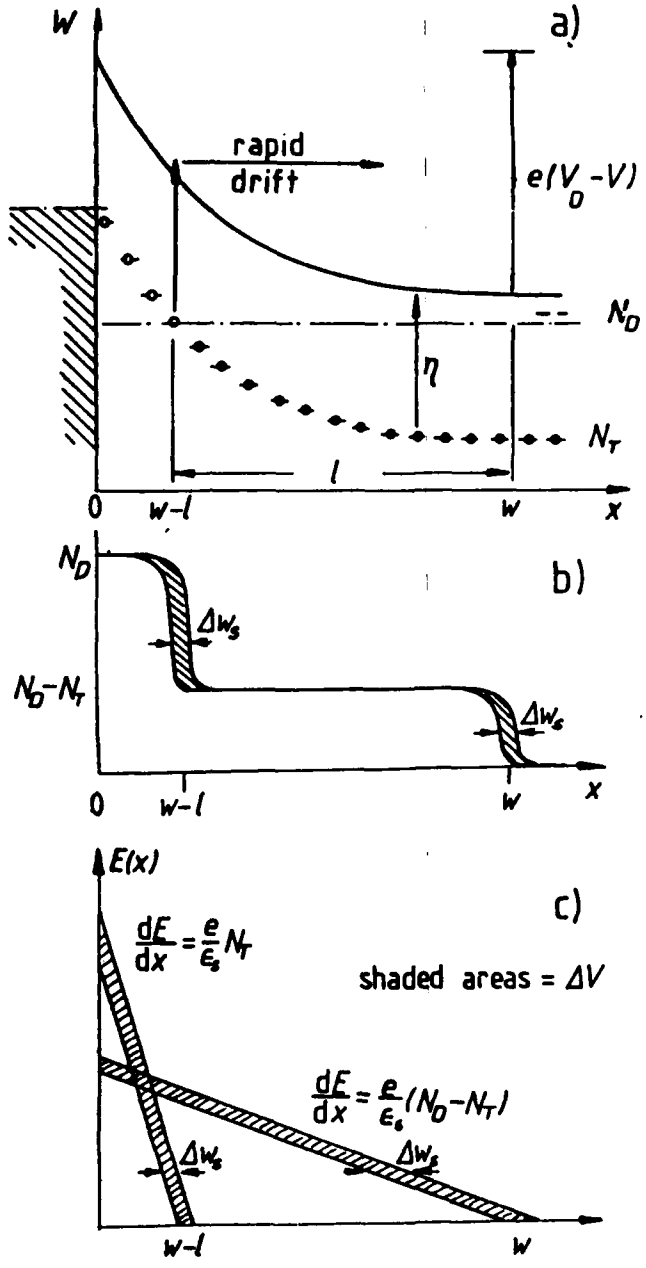

Figure 1

The band diagram of a Schottky barrier on n-type semiconductor, (a) showing a deep trapping level at a depth η below the conduction band. The space charge width is w with a diffusion potential V_D and an actual barrier height $e(V_D-V)$, where V is the applied bias. The deep level cuts the Fermi level at a distance l from the edge of the space charge region. Diagram

(b) shows the distribution of space charge and the change arising from a small change of the applied bias ΔV causing a shift of the bands by Δw_s. Diagram

(c) gives the change of the electric field, the shaded areas giving the change of potential.

In the idealised situation in which the response of deep levels may be assumed to be exponential in time - which is implicitly the case in most theoretical approaches such as Schockley Read-Haines and others, the frequency response of the deep levels would correspond to the classical dielectric Debye model. We have reported repeatedly that this behaviour is hardly ever seen and that the consequences of this should be faced in terms of a modified theory of trapping and recombination.

Whatever the detailed time- and frequency-dependence of the trapping processes, the presence of a deep level gives rise to a dispersion of the barrier capacitance and to the corresponding loss in the low-frequency region of the spectrum and the magnitude of the dispersion. ΔC is a function of the degree of compensation of the semiconductor.

In addition to this deep level dispersion which may be regarded as a classical effect, one expects in Schottky diodes a direct-current (dc) contribution to dielectric loss, G_b/ω, where G_b is the dc conductance of the barrier arising from "prompt" or non-delayed transitions of electrons over the barrier potential. What is not expected classically is any form of low-frequency dispersion (LFD) which is described in detail in I and which must be associated with interfacial processes at the metal-semiconductor boundary, possibly involving some oxide layer sandwiched between them. These strongly dispersive processes are also closely associated with negative capacitance effects, reported in I and described in detail in the present report. We also note for the first time the presence of very slow relaxations in the barrier responses - extending over many hours or days - with gradual transitions from LFD to negative capacitance responses. These effects cannot be understood in terms of any classical models and they suggest that Gallium Arsenide Schottky diodes suffer from certain instabilities which may well be associated with structural changes near the interface and which influence the dielectric response in a very sensitive manner. We have already suggested that the presence of LFD is evidence of "electrochemical" as distinct from purely electrostatic processes [1,2]. The anomalies reported here draw attention to the existence of phenomena in GaAs Schottky diodes which are not understood and probably not suspected.

CLASSICAL ANALYSIS OF SCHOTTKY DIODES

With reference to Figure 1 we make the usual assumption of "abrupt charge distribution" which consists in ignoring the gradual tailing off of the potential and of carrier density at the edge of the space charge region at $x = w$. We believe that any consequences of this approximation are not important in the present context and, in particular, are not likely to influence the *frequency spectrum* of our responses, as distinct possibly from some minor adjustment of amplitude factors in the analysis. The solution of the space charge equation leads then to the classical parabolic band bending near the interface and we note that the functional dependence on distance from $x = w$ towards the interface is *invariant* with respect to the bias V, which merely affects the value of the boundary coordinate w. This means that the position of the crossing-over of the Fermi level with the trap level, at a distance l from w, is also invariant and thus l is independent of V and of temperature. Therefore the effect of changing bias is to shift the entire band diagram by changing the boundary w. These considerations remain valid whatever the distribution of charge in the space charge region, provided it rémains unchanged with bias, so that at sufficiently slow changes of bias the deep traps respond fully and the only variation is in the boundary value of the potential at $x = 0$, which determines V_D. For rapid small-signal changes, on the other hand, there is no change in the occupancy of the trapping states.

The physical origin of the barrier V_D may be due to one of two causes, or a combination of both. On the one hand, in the ideal situation in which there are no surface states on the semiconductor, the difference of metal and semiconductor work functions wholly determines $eV_D = \phi_m - \phi_s$ as shown in Figure 2a. In the opposite extreme, Figure 2b, the Fermi level at the semiconductor surface is pinned by a high density of surface states at an energy ζ_s and $eV_D = \zeta_s - \zeta$, irrespective of the metal and semiconductor work functions. While the actual situation may correspond to some intermediate case, the important point to note is that neither ϕ_m nor ζ_s are likely to be significantly dependent on temperature, so that the only temperature-dependent parameter in V_D is the bulk position of the Fermi level ζ.

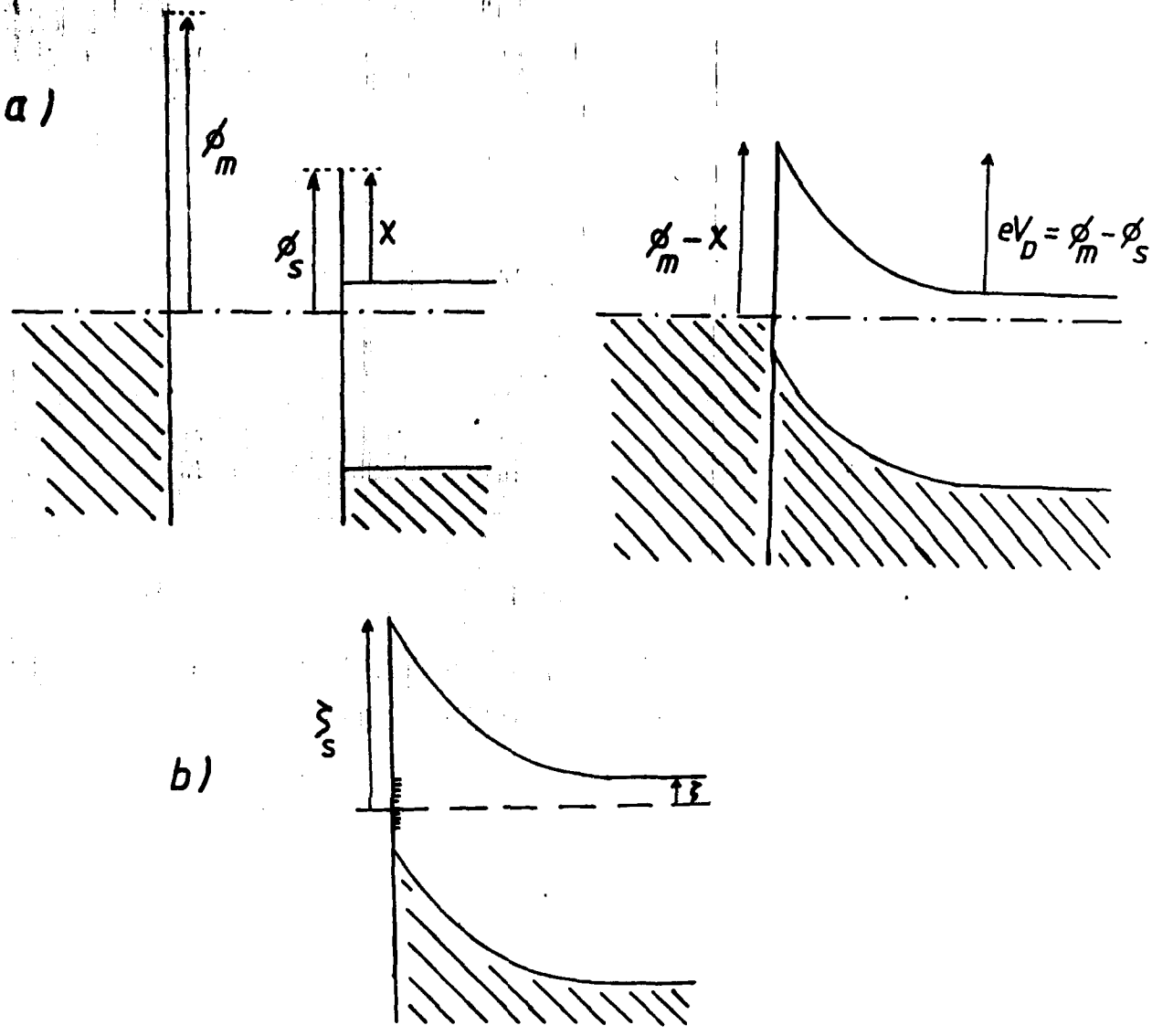

Figure 2

The formation of the barrier potential V_D under the action of
(a) the contact potential difference between the semiconductor and the metal in the absence of surface states, and
(b) the pinning of the Fermi level by a high density of surface states.

The integration of Poisson's equation for the space charge region gives the following result

$$e(V_D - V) = (e/\varepsilon)\ [(N_D - N_T)\ w^2 + N_T(w - l)^2]/2 \qquad (1)$$

A small steady state incremental bias ΔV results in an increase of w by Δw_s which is given by

$$\Delta V = (e/\varepsilon)\ (N_D w - N_T l)\ \Delta w_s \qquad (2)$$

The corresponding change of charge in the space charge region is $\Delta Q = eN_D\ w_s$ and this defines the low-frequency capacitance

$$C_{lf} = \Delta Q/\Delta V = (\varepsilon/w)[1 - (N_T l/N_D w)] \qquad (3)$$

If the incremental bias is applied at a sufficiently high frequency so that the deep traps cannot change their occupancy, the high-frequency changes are

$$\Delta V = (e/\varepsilon)\ (N_D - N_T)\ w\ \Delta w_f \qquad (4)$$

$$\Delta Q = e(N_D - N_T)\ \Delta w_f \qquad (5)$$

where Δw_f denotes the fast-response change of Δ. The corresponding high frequency capacitance is

$$C_{hf} = \varepsilon/w \qquad (6)$$

which is what would obtain in the absence of deep levels in a space charge region of depth w, but we note that w is itself a function of deep level density and may be obtained in the following manner from eqn (1). The expression for l is

$$l = [2\varepsilon n/e^2(N_D - N_T)]^{\frac{1}{2}} \qquad (7)$$

and defining dimensionless parameters

$$m = w/l > 1,\ s = N_T/N_D < 1,\ \mu = e(V_D - V)/\eta > 1 \tag{8}$$

we obtain the following quadratic equation for w/l

$$m^2 - 2sm + s - \mu(1 - s) = 0$$

which has the solution, bearing in mind that $m > 1$,

$$m = s + [s^2 - s + \mu(1 - s)]^{\frac{1}{2}} \tag{9}$$

where s is the fixed compensation parameter and the only bias, and temperature dependence arises from the ratio μ of the effective barrier height over the deep trap energy η.

It is now possible to determine the ratio

$$\frac{\Delta C}{C_{nf}} = \frac{1}{m/s - 1} \tag{10}$$

The form of the result as a function of the parameters μ and s is given schematically in Figure 3, showing that large ratios of incremental capacitance are expected for heavily compensated samples, with increasing temperature and forward bias, while small values are obtained in other conditions.

The voltage dependence of the capacitance is, in principle, an important factor in determining the impurity density in the system under investigation. In the absence of compensation by deep levels there is the simple relationship

$$\frac{1}{C^2} = \frac{2}{\varepsilon\, eN_D}\ (V_D - V) \tag{11}$$

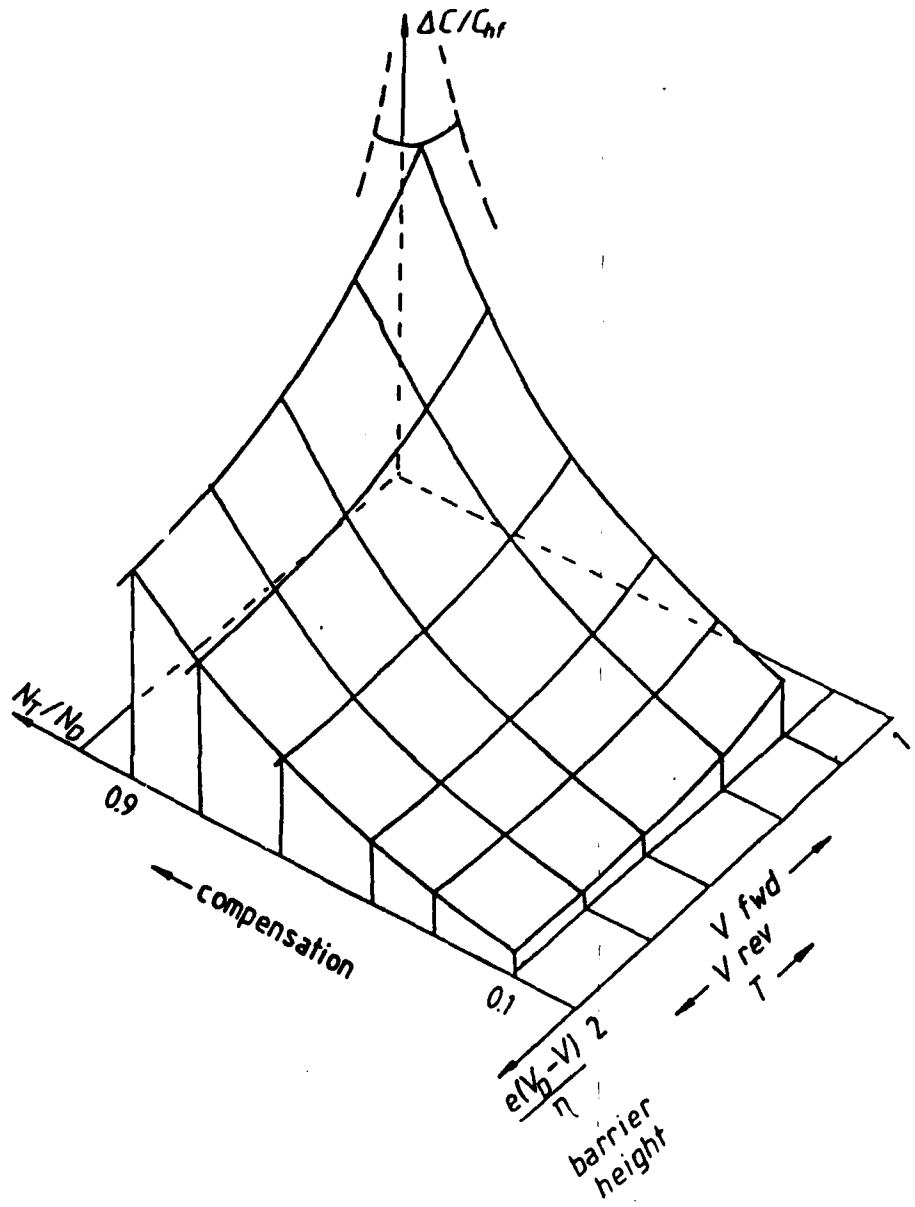

Figure 3

A schematic representation of the incremental capacitance in relation to the high-frequency capacitance, $\Delta C/C_{hf}$, as a function of the degree of compensation N_T/N_D and of the relative barrier height $e(V_D-V)/\eta$. The sense of increased forward and reverse bias and of rising temperature is indicated.

so that a plot of $1/C^2$ against V gives a straight line of slope that is inversely proportional to the donor density. No such simple relationship exists in the case where compensation is present and where there is dispersion between high and low frequencies in the value of the capacitance. There is insufficient information in the value of the high-frequency capacitance against voltage, when the degree of compensation is not known. There is, therefore, no point in plotting the reciprocal capacitance in the manner of eqn (11).

EXPERIMENTAL RESULTS

We have investigated in detail three types of Schottky diodes on GaAs with varying densities of donor impurities, as follows:

Diode No. 1	N_D =	1.45	10^{17} cm^{-3}
2		2.0	10^{16}
3		1.4	10^{15}

The active layers are epitaxially grown on n^+ (2 10^{18} cm^{-3}) buffer layers on n^+ substrates. Nothing is known of the extent of compensation in these samples but it may be presumed that the less heavily doped samples are effectively more strongly compensated. The Schottky electrodes are aluminium.

Measurements were carried out using the equipment and procedures described in I and the presentation of results follows similar lines.

The data for the most heavily doped sample No.1 are collected in Figure 4 as compilations of responses for individual temperatures in the range 294 - 373K, all with 0.1V RMS signal and with, respectively, 0.2V forward, zero and 0.2V reverse bias. The zero bias data show a clear dispersion associated with deep level emission, with an activated frequency shift corresponding to an energy of 0.66 eV and with an amplitude variation with temperature which is in qualitative agreement with the analysis of Figure 3. The value of C_{hf} corresponds clearly to a Schottky barrier and there is no evidence at all of the

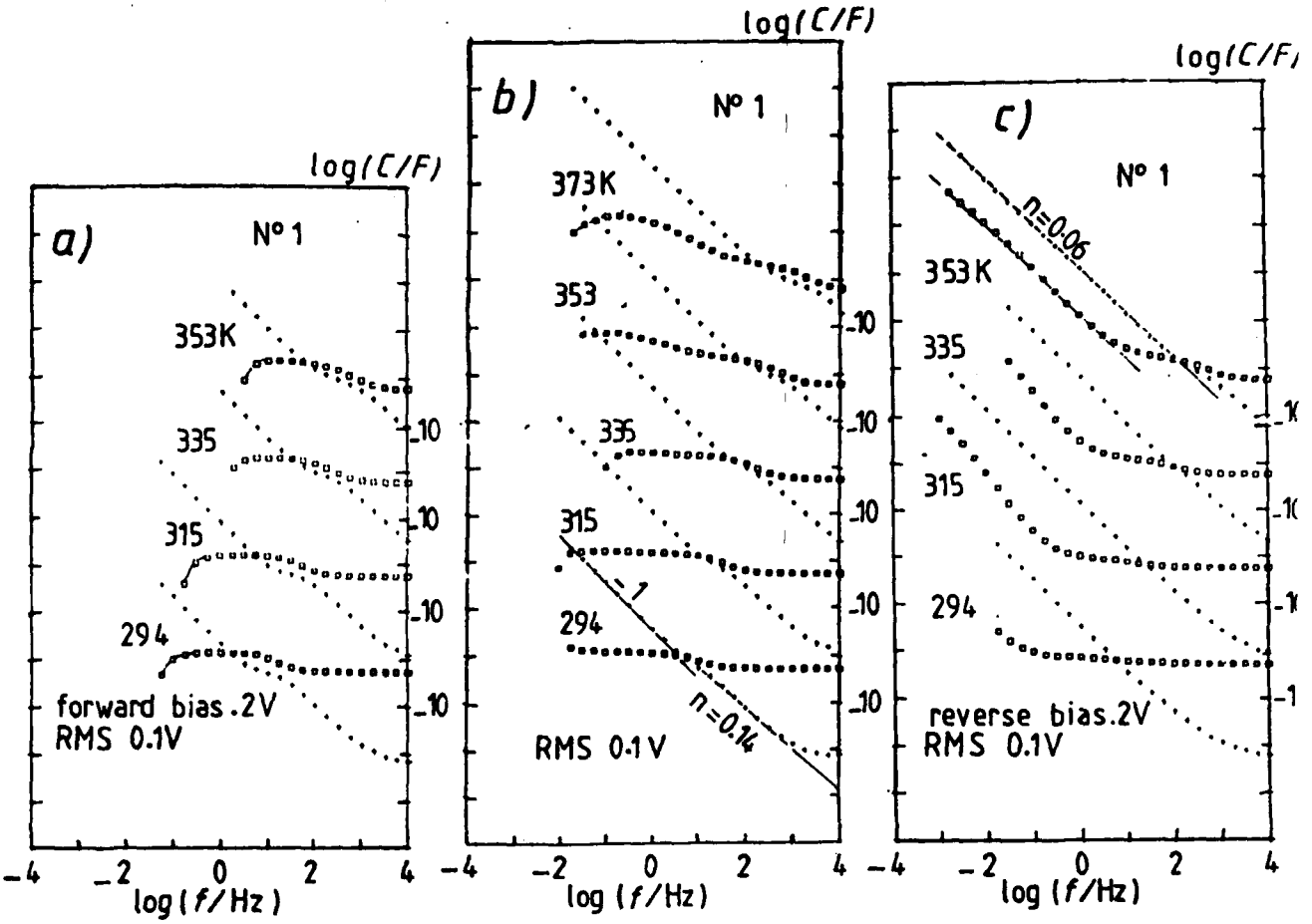

Figure 4

The dielectric response of diode No.1 showing the effect of temperature on the real (□□□□□□) and imaginary (++++++) components of the complex capacitance. Signal amplitude 0.1V RMS, bias 0.2V forward in (a), zero in (b), and 0.2V reverse in (c). The -1 slope and the values of the exponent n are indicated, the two slopes in (c) are in Kramers-Kronig compatible positions. Consecutive sets of data for individual temperatures displaced vertically by two decades for clarity.

limiting action of series resistance which was so characteristic of the semi-insulating samples in I. The loss associated with the deep level dispersion shows a marked deviation from the Debye characteristic, with the exponent $n = 0.14$ and a clear tendency to saturation at the highest frequencies. Up to this point the behaviour may be said to be classical with the position of the loss with respect to dispersion of $C'(\omega)$ suggesting that the dc leakage conductance of the barrier is comparable with the series conductance of the bulk material.

A novel feature visible at zero bias and becoming dominant at forward bias is the appearance of a clear tendency to negative capacitance at the lowest frequencies which is shown as a compilation of responses with increasing forward bias in Figure 5. Only the highest bias data give the full negative branch, with the negative value of the exponent $n = -0.11$ corresponding to the Kramers-Kronig compatible positions of the real and imaginary components. The frequency at which the shift to negative values takes place moves rapidly to higher values between 0 and 0.2V bias and afterwards remains almost constant up to the highest bias of 1V. The frequency of the deep level emission dispersion also moves slightly with increasing forward bias towards high frequencies, the total shift between 0 and 1V being approximately one decade. It would appear that this process is physically separate from the onset of negative capacitance, and we do not at present understand its mechanism.

A further novel feature of the low-frequency response appears at higher temperatures in the form of a tendency to LFD which is, however, over-taken by the negative capacitance trend already mentioned.

With negative bias, on the other hand, the low-frequency behaviour becomes dominated by a steadily developing LFD, with an exponent $n = 0.06$ at 353 K, and with full three decades of capacitance dispersion.

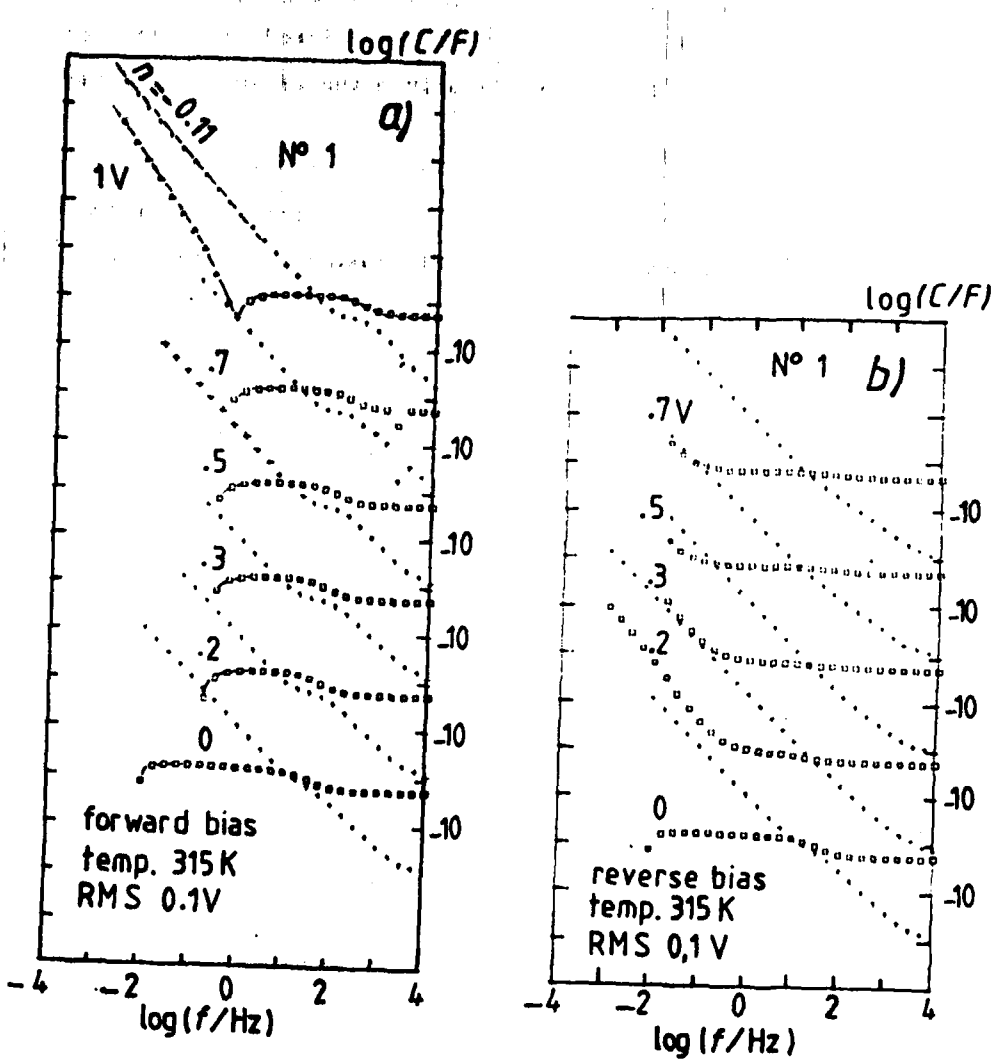

Figure 5

(a) The effect of increasing forward bias on diode No.1 at 315 K, signal amplitude 0.1V RMS. The 1V bias data show the negative capacitance following a Kramers-Kronig compatible dependence on frequency with a negative value of the exponent $n = 0.11$.

(b) Similar data for reverse bias at 315 K.

It is remarkable that the full swing from LFD to negative capacitance is achieved with a steady bias as low as 0.2V reverse and forward, respectively, which may be regarded as very small bias in comparison with either the band gap or the diffusion potential V_D.

The normalisation of the zero bias data with respect to temperature is shown in Figure 6. The high-frequency branch does not show any change of spectral shape with temperature and an activation energy of 0.66 eV is obtained from the frequency shift. The same plot shows a clearly changing spectral shape of the low-frequency part, with the somewhat surprising opposite trends in the real and imaginary components - while $C'(\omega)$ shows a strong rise before the negative capacitance branch is reached, the loss shows a reduction.

The response of diode No.2 is given in Figure 7 as a scan over a wide temperature range 193 - 363 K at zero bias, and also as a function of bias changing from -0.7V to + 0.4V at 348 K. The nature of the response is very similar to that of diode No.1 with the activation energy of the loss peak of the dispersion equal to 0.8 eV at high temperatures and 0.35 eV at lower temperatures. The amplitude of ΔC conforms qualitatively to the expected behaviour shown in Figure 3.

We now come to the least heavily doped diode No.3 which is, therefore, likely to be relatively more compensated. The data were taken at 300 K only and two samples were studied, referred to as 3.1 and 3.2. The data for diode 3.1 are shown in Figure 8 for a range of forward biases up to 3.0V, which may be regarded as very high in view of the fact that it exceeds the probable value of the barrier height of the order of 1V. While at zero bias there is no tendency to negative capacitance in the measurement window, from 0.5V onwards the trend is clearly developing with increasing transition frequency and also with a clearly rising frequency of deep level dispersion. The associated magnitude of ΔC is much larger in this diode than in any of the others, probably on account of its stronger compensation. One further feature has, however, become apparent in this investigation.

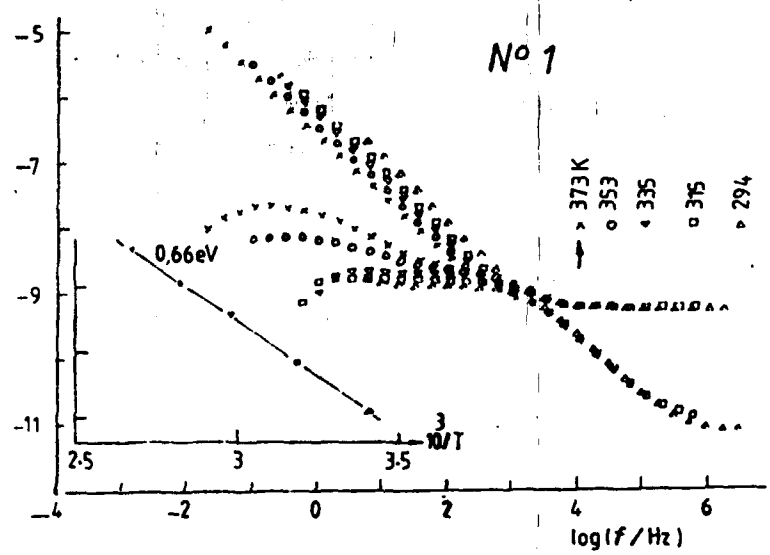

Figure 6

The normalisation of data for diode No.1 shown in Figure 4, giving an activation energy of 0.66V for the high-frequency process, and indicating a lower activation energy for the low-frequency process. The gradual evolution of the low-frequency capacitance is evident, rising initially and then falling towards negative values at higher temperatures.

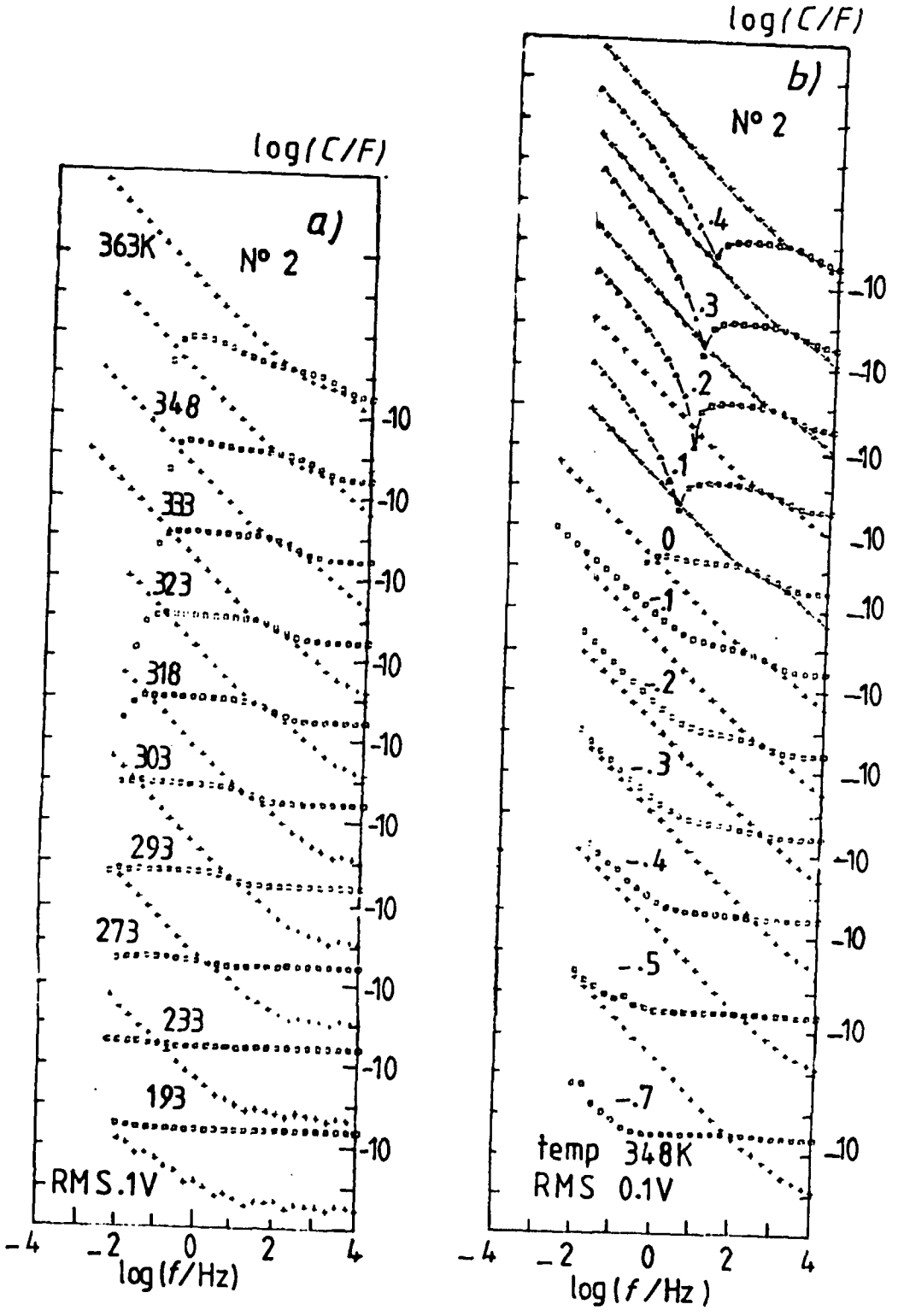

Figure 7

The evolution of the dielectric response of diode No.2. Diagram (a) gives the variation with temperature from 193 to 363 K, at zero bias, diagram (b) the evolution with bias from -0.7 to 0.4V at 348 K.

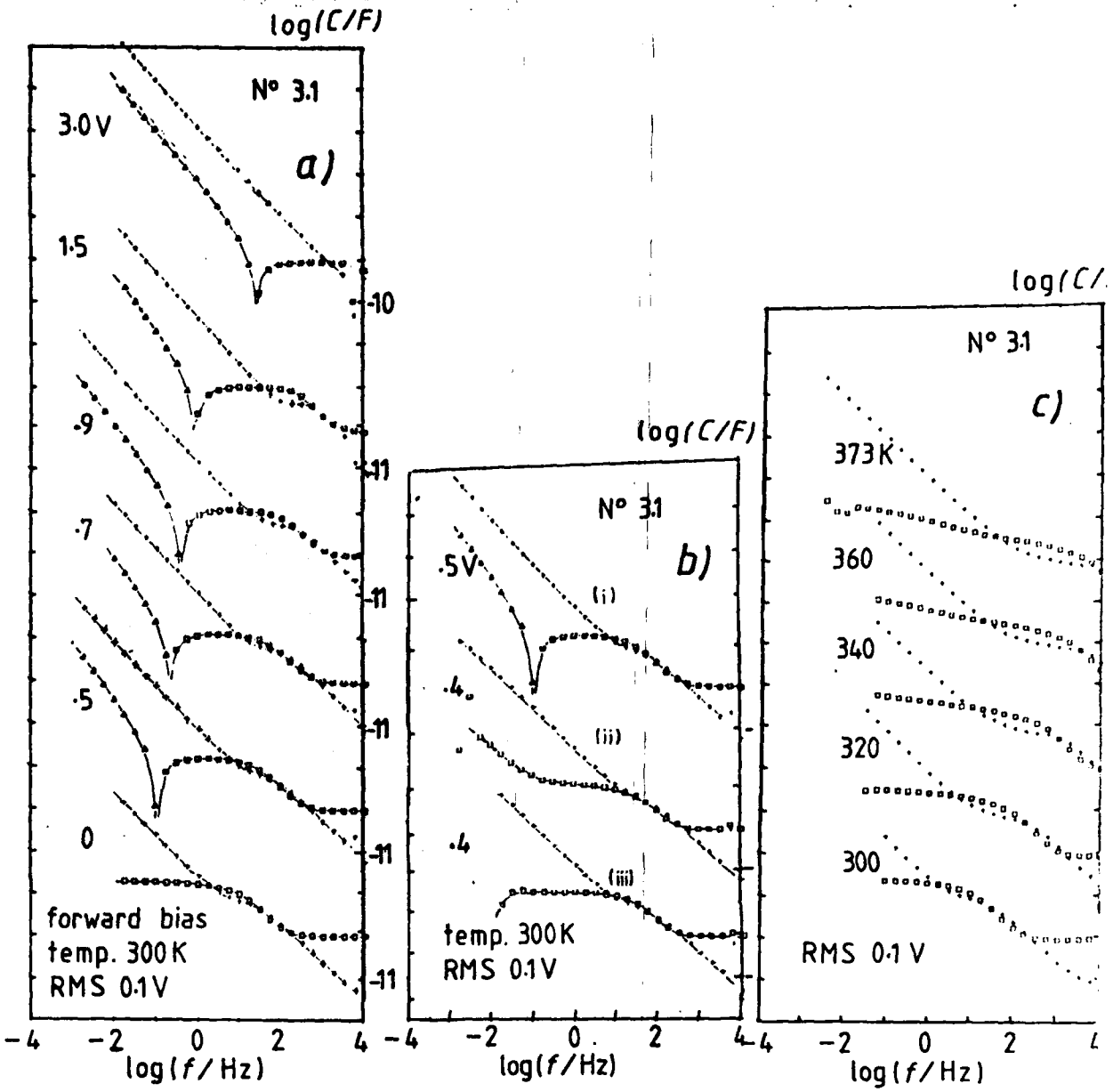

Figure 8

The dielectric response of one of the least heavily doped diodes, No.3.1.

(a) Shows the sequence of increasing forward biases, in the order in which they were measured. In diagram

(b) (i) reproduces the 0.5V bias response from diagram (a),

(ii) gives the 0.4V bias approximately 3 hours after the 3.0V bias run in (a),

(iii) repeats the 0.4V bias four days later.

(c) Shows the evolution of the response with increasing temperature and zero bias.

The sequence in which data were taken is as shown in Figure 8 from bottom to top. At 0.5V there is a clearly developed negative capacitance response. Immediately after the 3.0V bias run another scan was taken with 0.4V bias and this time we find a clear tendency to LFD, with no trace of negative capacitance. Four days later, the same scan was repeated at 0.4V and this time there is an incipient negative capacitance response which might be consistent with the original data as falling between the 0 and 0.5V bias. A final run at zero bias reproduces the initial zero bias response exactly.

These measurements reveal that the negative capacitance/LFD behaviour entails clear elements of "memory" in the system, whereby strong biasing in the forward direction gives rise to initially irreversible changes which take several days to clear.

A similar set of measurements on diode 3.2 shown in Figure 9 gave very similar responses, with the exception that the bias was taken as high as 4.8V. The novel feature here is the reversal of the sign $C'(\omega)$ back to positive, which is significant since one would not expect the negative values of capacitance to continue indefinitely to ever lower frequencies.

The appearance of negative capacitance is linked in our interpretation with the time-domain response in which the charging current under step-function excitation shows a period of *positive* or *rising slope*, sandwiched between the normal negative slope regions at short and long times. There are many possible explanations of this type of behaviour and they may be linked with gradual changes of space charge arising from double injection, or to gradual structural changes being effected by the passage of current. The structural argument is relevant in the case of GaAs since the EL2 centre is known to be associated with instabilities and our experimental evidence on the slow recovery shown in Figure 8 is directly relevant.

In order to test this point of view we have carried out a direct measurement of the charging currents as a function of time using

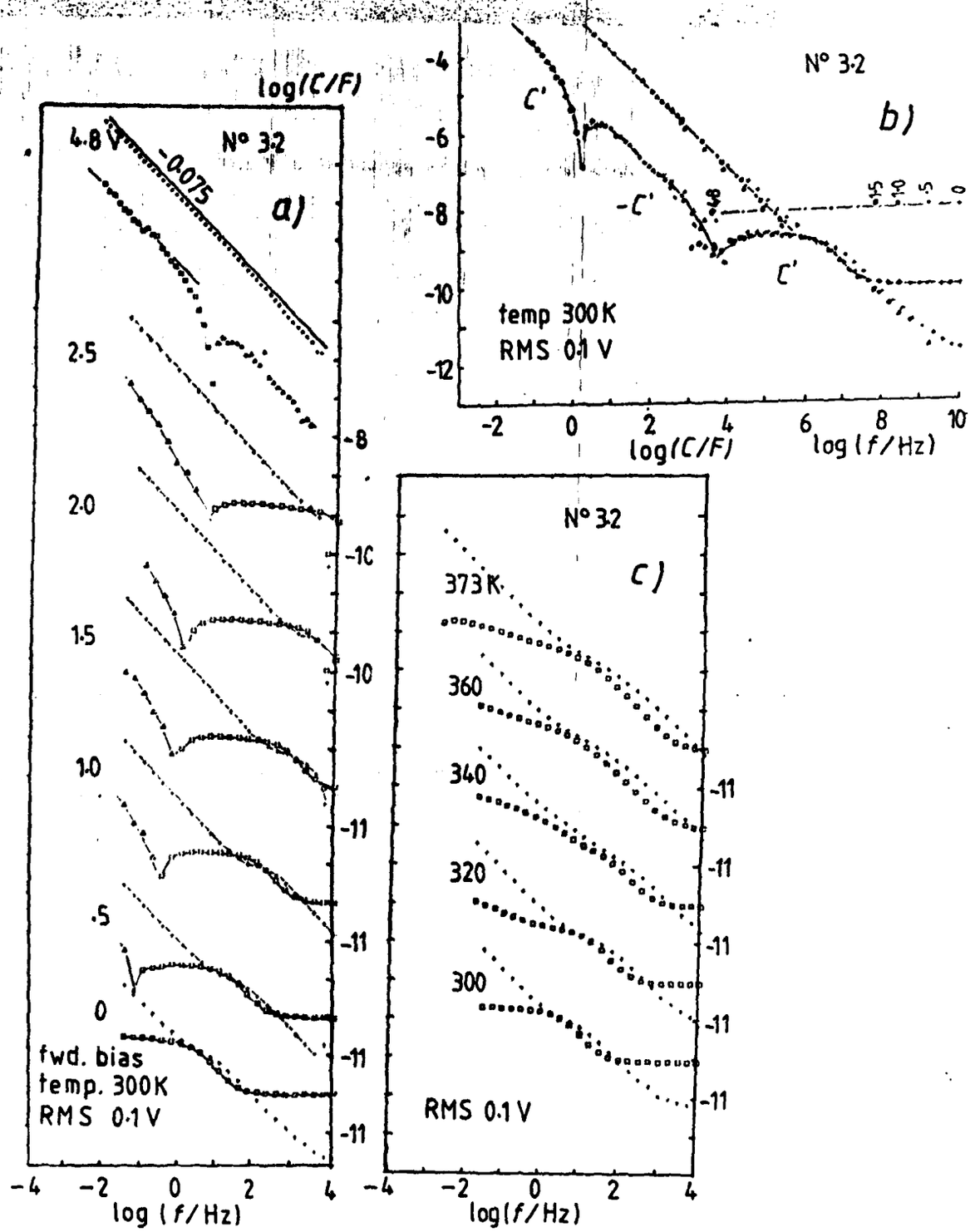

Figure 9

(a) The response of a similar diode, No.3.2, up to 4.8V forward bias, showing a return to positive values of capacitance at the lower frequencies with the highest bias.

(b) The normalisation of these data with respect to bias, showing the locus of translation.

(c) The evolution of the response with increasing temperature and zero bias.

our measurement equipment. The sensitivity of this equipment was too low to enable the discharging currents to be recorded, but the results of positive and negative charging step-function voltages are shown in Figure 10 which refers to diode No.1. It is clear that the negative pulse has a steady very slight negative slope, of the type consistent with LFD, while the positive pulse shows a region of strong rise of charging current after approximately 100 s. These results are in good qualitative agreement with the frequency domain response described earlier, although the quantitative agreement is less good because we are comparing *large signal* time domain responses with small-signal frequency domain measurements on an evidently non-linear system. For a more reliable comparison it would be required to apply a small step of voltage superimposed on a standing bias of the required magnitude, an experiment which has yet to be performed.

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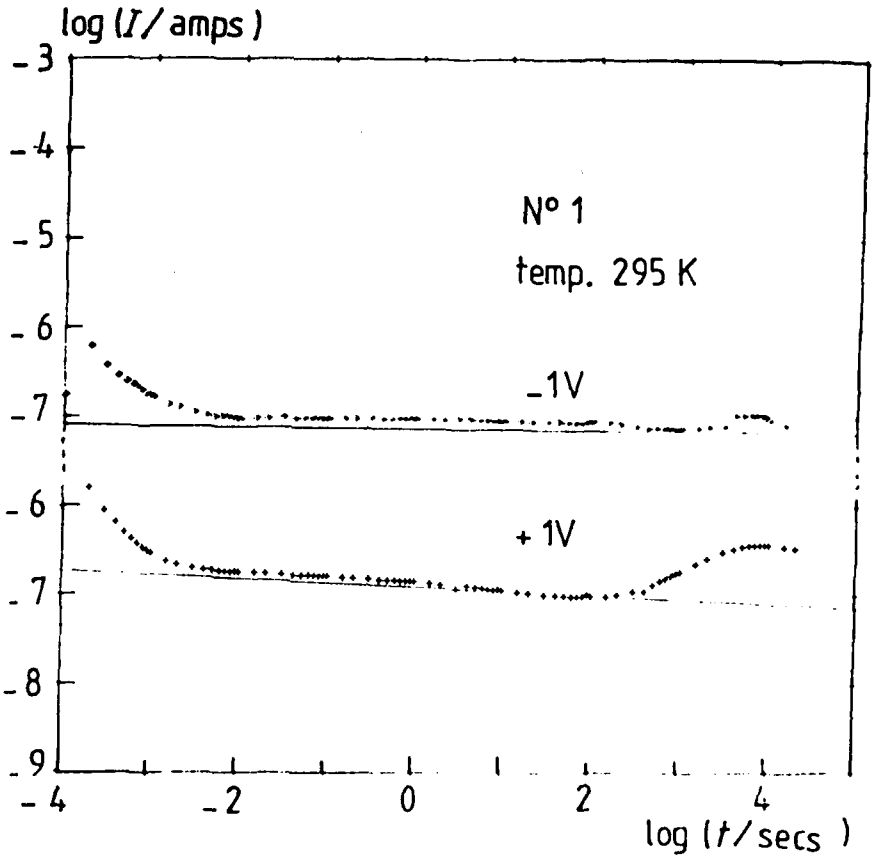

Figure 10

The time-domain charging current response of diode No.1 taken with 1V amplitude step voltage in the reverse direction (upper diagram) and forward direction (lower diagram). Both responses show a shallow negative slope corresponding to LFD in the frequency domain, but the forward bias data develop a strong rise of charging current at long times, consistent with the onset of negative capacitance at low frequencies. The corresponding discharge currents were too small to record.

CONCLUSIONS

The studies reported here of the dielectric response of Schottky diodes show conclusively that our understanding of the behaviour of these devices is very incomplete, and several aspects are unexpected. The most important among these is the low-frequency behaviour of the barrier response with zero bias and with relatively small forward and reverse biases. The appearance of negative capacitance phenomena and of low-frequency dispersion, respectively, suggests that the semiconductor-metal interface is a potentially unstable system in which electro-chemical reactions may be taking place and that these reactions are being influenced strongly by relatively small steady biases applied to the structure. The physical significance of these observations is not complete at the present time and more work is needed before definite conclusions can be drawn. However, it is clear that the detailed processes going on at interfaces of GaAs with metals, present questions which have not hitherto been even asked, let alone answered.

We were able to provide, for the first time, the time-domain confirmation of the negative capacitance interpretation, and the extent of the rising response of the charging current is most surprising.

The nature of the forward characteristics of these diodes is also not clear. The magnitude of the forward bias which has to be applied in order to obtain significant current flow is much larger than would be anticipated on the basis of the conventional approach to the diffusion potential in such systems.

We were able to show the existence of long-term recovery effects after the application of a high forward bias, which is of the same nature as the negative capacitance effects. This also confirms the metastability of the system.

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